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Near Infrared Absorption of Solutions of Hydroxides and Hydrolyzing Salts

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Absorption bands have been observed at 2.60μ, 2.30μ, 1.81μ, 1.30μ, 1.22μ, 1.04μ, 0.87μ, 0.79μ, 0.75μ and 0.67μ in aqueous solutions of hydroxides and hydrolyzing salts. From the behavior of the salt solutions the bands at 2.60μ and 1.81μ were found to be characteristic of the hydroxide molecule, while the band at 2.30μ was found to be characteristic of the OH ion. It was found that if the 2.30μ band, and the 3.65μ and 5.20μ bands previously observed were considered as fundamentals, the remaining bands observed could be classified as harmonics.

RECENTLY a study has been made of solutions of certain hydroxides and hydrolyzing salts[1] in the region from 2.8μ to 6.5μ. All bases showed intense bands at 3.65μ and 5.2μ, and from the absorption of the hydrolyzing salts it was concluded that these bands were due to changes in energy levels of the hydroxide molecules attached to water molecules. Plyler and Barr[2] have studied a number of acid solutions in the region from 1.7μ to 6.5μ and have found absorption bands at 2.4μ, and 5.5μ. Collins[3] observed bands at 0.96μ, 1.10μ and 1.26μ in alcoholic solutions of certain hydroxides, and Grantham[4] observed a band at 2.29μ in aqueous solutions of some hydroxides. A recent study by Plyler and Williams[5] of solutions of hydroxides in alcohol has revealed a number of bands not observed before. The present work was undertaken to see if other bands could be found in aqueous solutions in the near infrared, and to attempt through a study of hydrolyzing salts to obtain more information about the 2.29μ band previously observed.

The experimental method was the same as that used by Plyler and Barr. A quartz prism was used in the region from 0.60μ to 1.26μ and one of fluorite in the region from 1.26μ to 2.8μ. The cell thicknesses were: 2 cm for the range 0.6μ to 1.1μ; 0.5 cm for the range 1.10μ to 1.26μ; 0.01 cm in the range 1.26μ to 2.8μ. Cell windows for the entire region studied were of thin plate glass.

The first two curves in Fig. 1 show the absorption of 10N solutions of NaOH and KOH, the upper curve being for the former. The bottom curve is for 5N LiOH solution. It will be noticed that all of these curves show definite minima at approximately the same positions, at about 0.75μ, 0.79μ, 0.87μ, 1.04μ and 1.22μ. Another band at about 0.67μ was also found but is not shown in the figure. The lower intensity of the LiOH bands is due to the lower concentration. Fig. 2 shows the absorption of the same solutions in the region from 1.26μ to 2.8μ. Here it will be noticed that each solution shows intense bands with minima at 2.3μ and 2.6μ. There are

[1] E. K. Plyler and Walter Gordy, J. Chem. Phys. **2**, 470 (1934).
[2] E. K. Plyler and E. S. Barr, J. Chem. Phys. **2**, 306 (1934).
[3] J. R. Collins, Phys. Rev. **20**, 486 (1922).
[4] G. E. Grantham, Phys. Rev. **18**, 339 (1920).
[5] E. K. Plyler and F. D. Williams, J. Chem. Phys. **2**, 564 (1934).

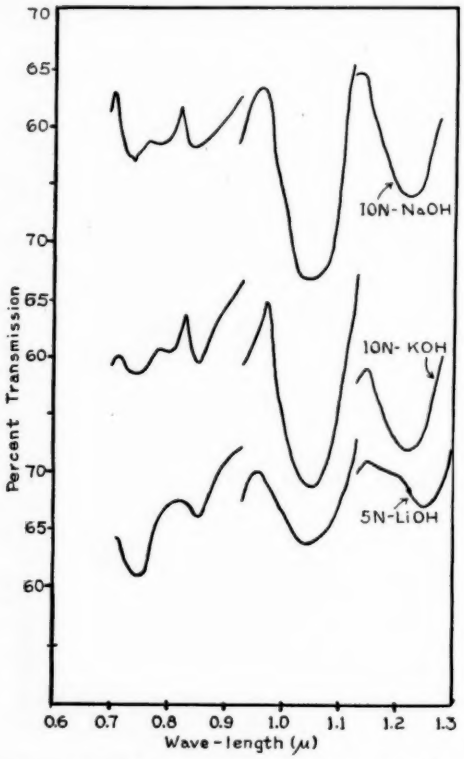

FIG. 1. Absorption in the region of 0.6μ to 1.26μ for aqueous solutions of hydroxides, cell thicknesses being 2 cm for the range 0.6μ to 1.1μ and 0.5 cm from 1.1μ to 1.26μ.

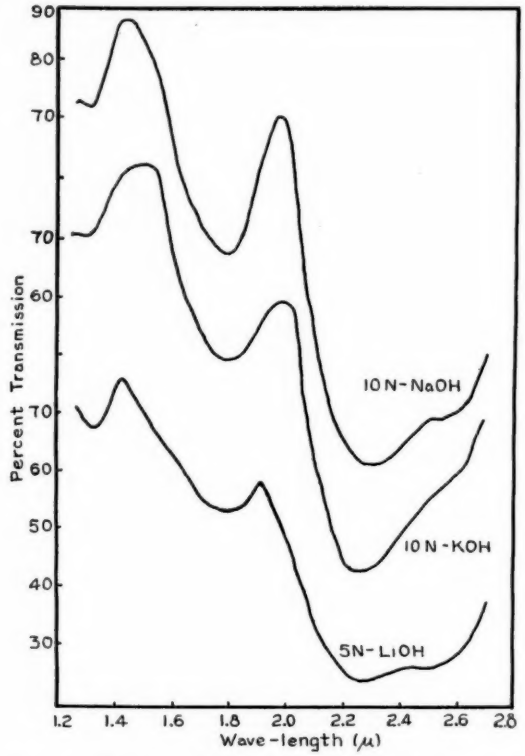

FIG. 2. Absorption in the region from 1.26μ to 2.8μ for aqueous solutions of hydroxides, cell thickness being 0.01 cm.

also definite bands in the regions of 1.3μ and 1.81μ. From the results of the study of hydrolyzing salts, it is possible to draw definite conclusions about the bands at 1.81μ, 2.3μ and 2.6μ. It will be observed in Fig. 3 that the salts which are basic in solution, namely, Na_2CO_3 and $NaC_2H_3O_2$, show strong absorption at 2.3μ; whereas, in the case of salts which give an acid reaction in solution, namely, $ZnCl_2$ and $ZnBr_2$, the absorption is much weaker in this region. Since this band has been shown to be due to the hydroxides the above mentioned variations in intensity of hydrolyzing salts indicate that the absorption is due to changes in energy levels between the OH ions and the water molecule. Oppositely, the bands at 1.81μ and 2.6μ are more intense for the salt solutions giving acid reaction and less intense for those which are basic in solution. This intensity variation is followed by all salts studied except $NaC_2H_3O_2$. The absorption of acetic acid solution was measured in this region, and was found to have bands which account for this discrepancy. This intensity change shows that the 1.81μ and 2.6μ bands are due to the hydroxide molecule. They are in the approximate positions for the first harmonics of the 3.65μ and 5.2μ bands reported by Plyler and Gordy, and shown by them to be due to the undissociated

TABLE I. *Classification of observed bands.*

Term	Frequency in cm^{-1} Cal.	Obs.	Wave-length in microns Cal.	Obs.
ν_1	1923	1923	5.20*	5.20
ν_2	2739	2739	3.65*	3.65
$2\nu_1$	3846	3846	2.60	2.60
ν_3	4348	4348	2.30*	2.30
$2\nu_2$	5494	5524	1.82	1.81
$3\nu_1$	5769		1.73	
$4\nu_1$	7692	7692	1.30	1.30
$3\nu_2$	8196	8196	1.22	1.22
$2\nu_3$	8695		1.15	
$5\nu_1$	9615	9615	1.04	1.04
$4\nu_2$	10989		0.91	
$6\nu_1$	11494	11494	.87	0.87
$3\nu_3$	12987	12645	.77	.79
$5\nu_2$	13698	13333	.73	.75

* Observed values taken as calculated.

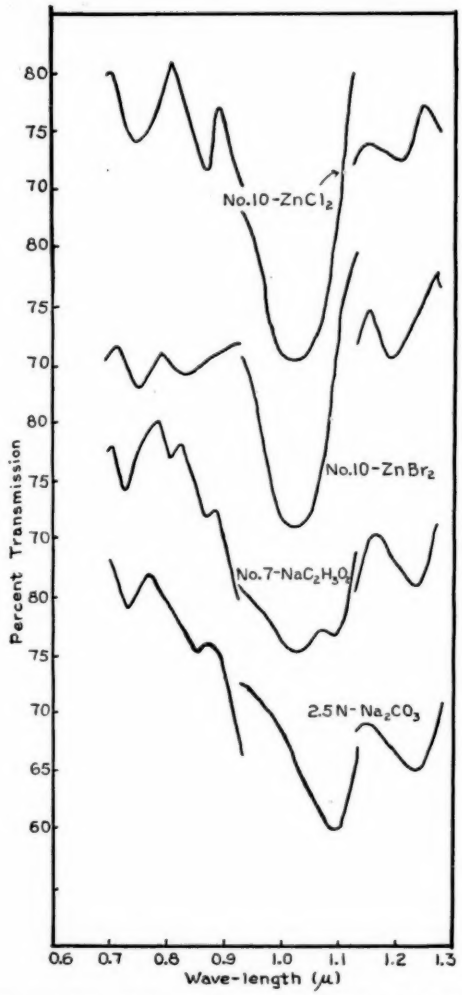

FIG. 3. Absorption in the region of 0.6μ to 1.26μ for aqueous solutions of hydrolyzing salts, cell thicknesses being 2 cm for the range 0.6μ to 1.1μ and 0.5 cm from 1.1μ to 1.26μ. *Note:* The curves No. 10 and curve No. 7 should read 10 N and 7 N, respectively.

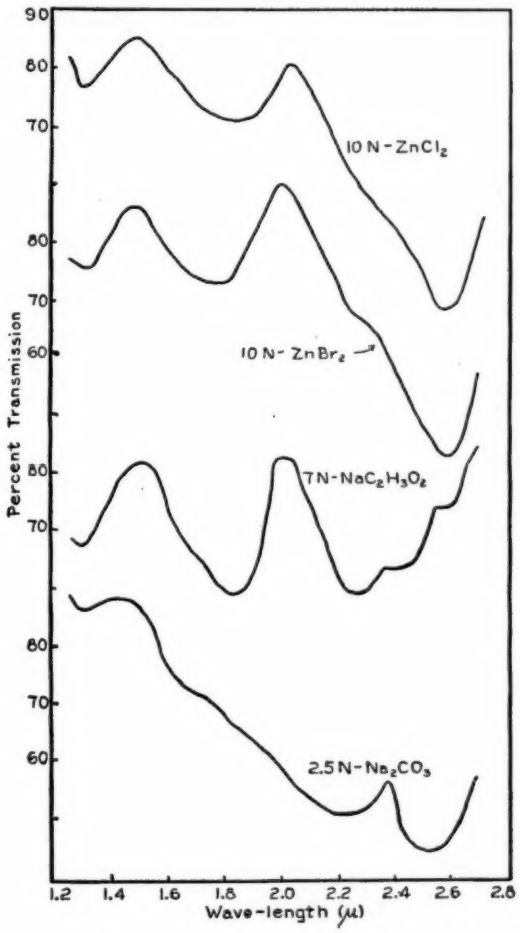

FIG. 4. Absorption in the region of 0.6μ to 1.26μ for aqueous solutions of hydrolyzing salts, cell thickness being 0.01 cm.

hydroxide molecule attached to water molecules. Because the 2.4μ acid band was between the 2.6μ hydroxide molecule band and the 2.3μ OH ion band, it was impossible, from the behavior of the salts, to conclude whether it was the acid molecule or ion attached to water. It was also impossible, because of low intensity and overlapping of higher harmonics, to apply this method of interpretation to the shorter wavelength bands. These harmonics were observed for all the salts and are shown in Fig. 4.

All bands observed for aqueous solutions of hydroxides were classified and are shown in Table I. The 2.3μ, 3.65μ and 5.2μ bands were considered as fundamentals, and it was found that all other bands could be classified as harmonics of these bands, with the exception of a small band at 0.67μ. The second harmonic of the 5.2μ band, the third harmonic of the 3.65μ band and the first harmonic of the 2.3μ band could not be resolved though higher harmonics of these respective bands were observed.

The writer wishes to express his thanks to Dr. E. K. Plyler who offered many helpful suggestions about this work.

The Raman Spectra and Molecular Constants of Phosphorus Trifluoride and Phosphine*

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The Raman frequencies of $PF_3(l)$ were found to be $\omega_1(1)$, 890 cm^{-1}; $\omega_2(1)$, 531 cm^{-1}; $\omega_3(2)$, 840 cm^{-1}; and $\omega_4(2)$, 486 cm^{-1}, indicating a regular pyramid structure of the molecule. Three frequencies were observed for $PH_3(l)$: 2306 cm^{-1}, 1115 cm^{-1} and 979 cm^{-1}. With the aid of electron diffraction data the standard virtual entropies of $PF_3(g)$, $PCl_3(g)$, $AsF_3(g)$, and $AsCl_3(g)$ at 25°C are calculated to be 64.2, 74.7, 69.2, and 78.2 cal./deg., respectively; that of $PH_3(g)$ is estimated to be 50.5 cal./deg. These data lead to the following free energies of formation at 25°C: $AsCl_3(g)$, −62,075 cal.; $PH_3(g)$, 2750 cal.; $PCl_3(g)$, −62,220 cal.

INTRODUCTION

THE thermodynamic constants and molecular structure of the volatile fluorides are most readily obtained, at the present time, from the results of Raman spectra and electron diffraction experiments. The free energy and entropy values so determined are not as accurate as those calculated from more complete spectroscopic data, but in general they are about as reliable as those resulting from equilibrium measurements. Then too, comparisons of the Raman frequencies and molecular sizes for a series of analogous substances give a measure of relative bond strengths and point to possible generalizations regarding bond angles and molecular shapes.

In the present paper are presented the results of an investigation on the Raman spectra of phosphorus trifluoride and phosphine, together with a discussion of their thermodynamic quantities and molecular structures.

We wish to express here our indebtedness to Dr. L. O. Brockway and Mr. F. T. Wall for permitting us to use as yet unpublished results of electron diffraction experiments made on phosphorus trifluoride, arsenic trifluoride and arsenic trichloride.

EXPERIMENTAL

The phosphorus trifluoride was prepared by the direct reaction between arsenic trifluoride and phosphorus trichloride.[1] The two liquids are not miscible, and the reaction is slow, but its rate was increased by adding a few drops of antimony pentachloride and by warming the mixture to 35°. In this manner 20 cc of liquid phosphorus trifluoride (m.p. −160°, b.p. −95°) was prepared in two hours. The resulting material was fractionated repeatedly and condensed into a Raman tube which was then sealed. To obtain the spectrum the tube was placed in a Dewar flask containing alcohol and solid carbon dioxide. The Dewar flask was silvered over one-half of its circumference in such a way that it formed a semi-cylindrical mirror.

Phosphine was prepared by treating calcium phosphide with water. A train of gas absorption bottles containing concentrated hydrochloric acid and water served to convert the lower phosphorus hydrides into phosphine. The gas was thoroughly dried by passing it repeatedly through traps cooled with solid carbon dioxide. The resulting material was condensed into a Raman tube which was then sealed off and placed in the above-described Dewar flask which contained alcohol and solid carbon dioxide.

Both the phosphorus trifluoride and phosphine were present as liquids under their own vapor pressures of 2 to 4 atmospheres. Good photographs were obtained in one and one-half to three hours with a water-cooled mercury arc in Pyrex as a source of radiation. The spectrum from gaseous phosphorus trifluoride was also photographed by using the 2537A line of mercury as a source of radiation. Three Raman lines were obtained. Considerable decomposition of the gas took place with the formation of a yellow solid.

* Publication No. 423.

[1] Ruff, *Die Chemie des Fluors*, p. 28, Springer, Berlin, 1920.

TABLE I. *The Raman spectra and molecular constants of phosphorus trifluoride, phosphine and analogous trihalides.*

Substance	$\omega_1(1)$ (cm^{-1})	$\omega_2(1)$ (cm^{-1})	$\omega_3(2)$ (cm^{-1})	$\omega_4(2)$ (cm^{-1})	M–X (A)	X–X (A)	β	$I_1\times10^{40}$ ($g\cdot cm^2$)	$I_2\times10^{40}$ ($g\cdot cm^2$)	S^*_{298} cal./deg.
PH_3†	2306(10)	979(2)		1115(1)	(1.45)	(2.23)	(100°)	(8.26)	6.22	50.5±1
PF_3	890(10)	531(3)	840(10)	486(3)	1.56	2.37	99°	176.0	106.6	64.2±2
$PF_3(g)$	893(5)		851(5)	487(7)						
PCl_3(2)	510(10)	257(10)	480(2)	190(10)	2.02	3.09	100°	558.3	314.7	74.7±3
AsF_3(3)	707(10)	341(2)	644(9)	274(4)	1.73	(2.65)	(100°)	220.0	144.8	69.2±2
$AsCl_3$(2)	410(10)	193(6)	370(6)	159(8)	2.18	3.36	101°	661.8	402.0	78.2±3

Numbers in parentheses adjoining frequency values are relative intensities. Numbers in parentheses adjoining ω's are multiplicities. M–X and X–X are interatomic distances. β is the bond angle formed by two X-atoms and the M-atom. I_1 and $I_2(=I_3)$ are moments of inertia about the symmetry axis and the axis $\perp$ symmetry axis, respectively. S^*_{298} is the virtual entropy of the vapor at one atmosphere and 25°C.
† In the case of phosphine the assignment of frequencies is provisional.

EXPERIMENTAL RESULTS AND DISCUSSION

The results of the experiments are presented in Table I together with various derived quantities. For comparison the corresponding values for phosphorus trichloride, arsenic trifluoride and arsenic trichloride are also given.

The assignment of the frequencies of the trifluoride to the modes of vibration was made by comparison of the spectrum from the trifluoride with that from the trichloride. In the latter case the assignment is based on polarization experiments.[2] The lines ω_2 and ω_4 are quite sharp and narrow while ω_1 and ω_3 are broad with a width of about 30 cm^{-1} each. The three lines found for gaseous PF_3 are all sharp.

If the atoms in phosphorus trifluoride occupy the corners of a regular triangular pyramid then the four lines ω_1, ω_2, ω_3 and ω_4 are permitted by the Raman selection rules.[3,4] Any deviation from regularity of the structure would lead to splitting of the frequencies ω_3 and ω_4 which have multiplicities of two each, and no splitting was observed. Since four lines were observed it may be concluded that the regular triangular pyramidal structure is to be ascribed to phosphorus trifluoride. The results of the electron diffraction experiments are in complete agreement with this conclusion.

Although the Raman selection rules permit four lines in the case of phosphine if it is assumed, as is probably correct, that the atoms occupy the corners of a regular triangular pyramid, only three were observed. That at 2306 cm^{-1} was remarkably intense and fairly sharp; another at 979 cm^{-1} was much weaker and quite sharp, while the third line at 1115 cm^{-1} was weaker still and somewhat diffuse. These lines correspond closely to three bands observed in the infrared,[5] namely, 2327, 990–992.5 and 1121 cm^{-1}, the lack of perfect agreement being doubtless due to the fact that the Raman frequencies were obtained from the liquid, while the infrared absorption bands were obtained from the gas. If one assumes with Fung and Barker that the two bands at 990 and 992.4 cm^{-1} are fundamentals, then the Raman line 979 cm^{-1} consists of two unresolved fundamentals. In this manner the fourth permitted Raman frequency would be accounted for. Under this assumption Fung and Barker were led to the conclusion that the phosphine molecule is a spherical top, and since the moment of inertia about the axis perpendicular to the symmetry axis[6] is 6.22×10^{-40} $g\cdot cm^2$ the phosphorus bond angle would be $88\frac{1}{2}°$.

However, from Table I it is seen that the bond angles in PCl_3, PF_3 and $AsCl_3$ are 100°, 99° and 101°, respectively, and the results of Barnes, Benedict and Lewis[7] on ND_3 and NH_3 yield an angle of 108° for NH_3. These facts indicate that the bond angle is nearly an invariant for the trivalent compounds of the fifth group elements. According to this empirical generalization the bond angle in phosphine would be about 100°, and the molecule becomes a symmetrical top with a moment of inertia about the symmetry

[2] Cabannes and Rousset, Ann. de physique **19**, 229 (1933). The internuclear distances for PCl_3 are due to Wierl, Ann. d. Physik **8**, 521 (1931).
[3] Yost and Sherborne, J. Chem. Phys. **2**, 125 (1934).
[4] Debye, *The Structure of Molecules*, Blackie and Son, Ltd., London, 1932. Cf. the article by Placzek, p. 86. E. B. Wilson, Jr., J. Chem. Phys. **2**, 432 (1934).
[5] Fung and Barker, Phys. Rev. **45**, 238 (1934).
[6] Wright and Randall, Phys. Rev. **44**, 391 (1933).
[7] Barnes, Benedict and Lewis, Phys. Rev. **45**, 347 (1934).

axis of 8.13×10^{-40} g·cm². The 990–992.4 cm^{-1} band would then arise from a single fundamental vibration in which the phosphorus atom passes through the triangle formed by the hydrogen atoms as has been observed with ammonia.[8] The fact that no doubling is observed in the pure rotation spectrum is due to the circumstance that the separation (approximately 0.0007 cm^{-1}) would be too small to be resolved. The fact that the fourth Raman line is not observed can be ascribed simply to a lack of sufficient intensity; this phenomenon is common in the case of molecules containing hydrogen.

Thermodynamic Constants

The calculated entropies are given in the last column of Table I. The Raman frequencies obtained from liquids are generally lower than those obtained for the same substances in the gaseous states. The vibrational entropies calculated will, accordingly, be too great, and the magnitude of the deviations have been indicated in the table.

In the case of $AsCl_3$ complete thermal data are available for free energy calculations.[9] For $AsCl_3(l)$ and $AsCl_3(g)$ the heats of formation are 72,470 cal. and 65,110 cal., respectively, and the calculated standard free energies of formation at 25° are −64,550 cal. and −62,075 cal., respectively. Equilibrium measurements in progress at this laboratory give a preliminary value of −58,500 cal. for $AsCl_3(g)$. The agreement is satisfactory. No thermal data are available for AsF_3 and PF_3.

A number of determinations have been made of the heat and free energy of formation of phosphine but none of them are free from objections. The entropy of solid white phosphorus has not been determined. Preuner and Brockmöller[10] have made equilibrium measurements on the reaction $P_4(g)=2\,P_2(g)$ over the temperature range 800°–1200°. Duncan and Macrae[11] have made careful vapor pressure measurements on solid white phosphorus and the vapor is known to consist of P_4.

Herzberg[12] has determined both the moment of inertia and the vibrational energies of P_2 in the normal electronic state, thus making possible the calculation of a reliable value for the entropy. An estimate has been made of the empirical heat capacity equation for P_4. The results are as follows:

$$P_4(g)=2\,P_2(g) \qquad (1)$$

$\Delta H_{1000}=33{,}800$ cal. $\quad \Delta F^\circ_{1300}=5110$ cal.

$P_2(g)$, $C_P=7.4+0.001\,T$

$S^*_{298}P_2(g)=52.0$ cal./deg.

$P_4(g)$, $C_P=10.0+0.003\,T$

$\Delta H_T=31{,}400+3.00\,T-0.0006\,T^2$

$\Delta F^\circ_T=31{,}400-3T\log_e T+0.0006\,T^2+481\,T$

$\Delta H_{298}=32{,}250$ cal. $\quad \Delta F^\circ_{298}=26{,}300$ cal.

$$4\,P(s,\text{white})=P_4(g) \qquad (2)$$

$\Delta H_{298}=13{,}220$ cal. $\quad \Delta F^\circ_{298}=5850$ cal.

From these equations there is obtained the value 14.9 cal./deg. for the entropy of solid white phosphorus at 25°.

The reaction between $P_4(g)$ and hydrogen to give phosphine has been studied by Ipatiew and Frost.[13] They proved definitely that the reaction is reversible, but due to the experimental difficulties involved the heat of the reaction could not be determined as accurately as desired. Calorimetric determinations of the heat of formation of phosphine are not at all satisfactory. From the best existing data the following equations have been derived.

$$P_4(g)+6H_2(g)=4\,PH_3(g) \qquad (3)$$

$\Delta H_{700}=-22{,}100$ cal. $\quad \Delta F^\circ_{700}=37{,}100$ cal.

$PH_3(g)$, $C_p=8.04+0.0007\,T+5.1\times10^{-6}T^2$

$H_2(g)$, $C_p=6.50+0.0009\,T$

$P_4(g)$, $C_p=10.0+0.003\,T$

$\Delta H_T=-11{,}300-16.84\,T-0.0028\,T^2$
$\qquad +6.8\times10^{-6}T^3$

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[8] Morse and Rosen, Phys. Rev. **42**, 210 (1932); Dennison and Uhlenbeck, ibid. **41**, 313 (1932).

[9] E. Peterson, Zeits. f. physik. Chemie **8**, 611 (1891); Baxter, Bezzenberger and Wilson, J. Am. Chem. Soc. **42**, 1386 (1920); Yost and Sherborne, J. Chem. Phys. **2**, 125 (1934). In the latter article the moments of inertia and entropy values of $AsCl_3$, AsF_3 and PCl_3 are in error. These values as well as that for the free energy of formation of $AsCl_3$ have been recalculated and are given correctly in this paper.

[10] Preuner and Brockmöller, Zeits. f. physik. Chemie **81**, 129 (1913).

[11] Duncan and Macrae, J. Am. Chem. Soc. **43**, 547 (1921).

[12] Herzberg, Zeits. f. Physik **69**, 548 (1931); Phys. Rev. **40**, 313 (1932).

[13] Ipatiew and Frost, Ber. **63**, 1104 (1930).

$$\Delta F^\circ_T = -11{,}300 + 16.48\, T \log_e T + 0.0028\, T^2 - 3.4\times10^{-6} T^3 - 41.3\, T$$

$\Delta H_{298} = -16{,}400$ cal. $\Delta F^\circ_{298} = 5155$ cal.

From these equations and the heat and free energy of vaporization of white phosphorus given above, a second value of 15.5 cal./deg. for the entropy of solid white phosphorus may be calculated. The close agreement between the two independent values is, in some measure, fortuitous, and, judging from the entropies of other solid substances of similar nature, both values are possibly too high. Until more accurate data are available we shall take 15.0 cal./deg. as the entropy of solid white phosphorus at 25°.

It is now possible to calculate the thermodynamic constants for phosphorus trichloride. The heats of formation[14] and vaporization[15] of $PCl_3(l)$ are 75,900 cal. and −7620 cal., respectively, and the free energy of vaporization at 25° is 1080 cal. The following free energy equations may then be written:

$$P(s,w) + 3/2\ Cl_2(g) = PCl_3(l) \quad (4)$$

$\Delta H = -75{,}900$ cal. $\Delta F^\circ_{298} = -63{,}300$ cal.

$$P(s,w) + 3/2\ Cl_2(g) = PCl_3(g) \quad (5)$$

$\Delta H = -68{,}280$ cal. $\Delta F^\circ_{298} = -62{,}220$ cal.

[14] Berthelot and Longuinine, Ann. d. chim. phys. (5) **6**, 307 (1875); Thomsen, Ber. **16**, 37 (1883); J. Ogier, Comptes rendus **87**, 210 (1878).

[15] Regnault, Mem. de l'acad. Sciences, France **26**, 339 (1862).

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On the Infrared and Raman Spectra of Methyl Compounds

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An analysis of the resonance interaction between the vibrations ν_1 and $2\nu_4$ in the methyl halide molecules explains the appearance of the very intense extra band in the infrared and Raman spectra of these molecules. This degeneracy is evidently characteristic of the methyl group. A number of molecules involving the methyl group and exhibiting the phenomenon of the extra band are listed.

THE infrared spectra of the methyl halides has been found by Bennett and Meyer[1] to consist of four single or parallel bands and three double or perpendicular ones. The frequency and intensity relations between them seem to preclude the possibility that any one is an harmonic; nevertheless, the molecule must have only nine degrees of freedom for vibration, and not ten as apparently indicated. The Raman spectra do not resolve this difficulty, but rather tend to emphasize it. Methyl chloride and methyl bromide each have strong Raman lines corresponding to the four single frequencies. Only a few of the double frequencies appear in Raman observations, and these lines are weak as would be expected from Placzek's theory.

The positions of the infrared bands observed in gaseous absorption, and of the Raman lines obtained from the liquid, are listed in Table I. The designations by letter in the first column follow Bennett and Meyer, while the numerical subscripts are those of Dennison's analysis,[2] the even numbers corresponding to the double frequencies. Motions primarily involving the halogen atom are responsible for the frequencies ν_5 and ν_6, while in first approximation ν_3 and ν_4 correspond to oscillations of the carbon and ν_1 and ν_2 to those of the three hydrogen atoms. Consequently, ν_4, ν_2 and ν_1 are very insensitive to changes in mass of the fifth atom, and may be said to characterize the methyl radicle. There is no difficulty about the identification of D and G as ν_4 and ν_2, respectively, but either E or F seems at first superfluous.

Analysis indicates that the harmonic of a perpendicular band consists of two components,

[1] Bennett and Meyer, Phys. Rev. **32**, 888 (1928).

[2] Dennison, Rev. Mod. Phys. **3**, 280 (1931).

one parallel and one perpendicular, and the table shows that the harmonic of D should fall almost midway between E and F. This suggests that the parallel component of $2\nu_4$ may be in close resonance with ν_1, introducing an interaction which gives rise to a mixed wave function and a displacement of the two levels in opposite directions from their unperturbed positions. A similar situation has already been described in detail for CO_2.[3] Hence it seems quite natural to suppose that the bands E and F represent the set $(\nu_1, 2\nu_4)$, their intensities being comparable both in infrared and in Raman transitions, and considerably exceeding the expected intensity of a simple harmonic, as indicated by the absence of all such bands including the perpendicular component of $2\nu_4$ which does not partake of the interaction.

To determine the degree to which the vibrational levels ν_1 and $2\nu_4$ interact, and therefore the extent to which the resonance calculations must be introduced in the correlation of the infrared spectra of these molecules, we shall assume that in zeroth order approximation the degeneration is complete so that $\nu_1=2\nu_4$. The separation between the interacting frequencies will then be introduced as a part of the first order perturbing function, the remainder of which will consist of the terms of the cubic anharmonic potential giving the coupling between the two modes of vibration ν_1 and ν_4.

Accordingly, the zeroth order system of the modes of vibration is given by:

$$H_0=\frac{2\pi^2\nu_4}{h}\left[2p_\sigma^2+p_\rho^2+\frac{1}{\rho^2}p_\varphi^2\right]+\frac{h\nu_4}{2}[2\sigma^2+\rho^2],$$

where σ, ρ and φ are the dimensionless counterparts of the normal coordinates. σ specifies the single vibration ν_1, while ρ and φ measured in a plane perpendicular to the symmetry axis of the molecule describe the motion ν_4. Examination shows that the potential energy of vibration is an even function of ρ.

Forming and solving the wave equation, we find the zeroth order solution described by the energy

$$E_0=h\nu_4[2V_1+V_4+2],$$

and by the wave function

$$\Psi_0=\Psi^{V_1}{}_{(\sigma)}\Psi^{V_4 l}{}_{(\rho)}e^{\pm il\varphi}.$$

V_1, V_4, and l are the quantum numbers of vibration; and $\Psi^{V_1}{}_{(\sigma)}$ and $\Psi^{V_4 l}{}_{(\rho)}$ are, respectively, the Hermitian orthogonal function with argument σ and the associated Laguerre orthogonal function with argument ρ^2.

Setting $\Delta=\nu_1-2\nu_4$ we have, since the potential energy is an even function of ρ,

$$\lambda H_1=\frac{2\pi^2\Delta}{h}p_\sigma^2+h\left[\frac{\Delta\sigma^2}{2}+b\sigma\rho^2\right].$$

Replacing p_σ by $(h/2\pi i)(d/d\sigma)$, and making the substitution

$$d^2\Psi^{V_1}{}_{(\sigma)}/d\sigma^2=-[2V_1+1-\sigma^2]\Psi^{V_1}{}_{(\sigma)},$$

we have, finally:

$$\lambda H_1=h[\Delta\{V_1+\tfrac{1}{2}\}+b\sigma\rho^2].$$

Applying the first order perturbation to the system E_0, Ψ_0, the new description of the pair of interacting levels is set forth in Fig. 1, where the ψ's are the stabilized wave functions of the resultant levels.

The above analysis yields the solution

$$\Delta=\bar{R}-2\nu_4, \quad b^2=(\Lambda^2-\Delta^2)/2,$$

where $\bar{R}$ is the mean of the two infrared band

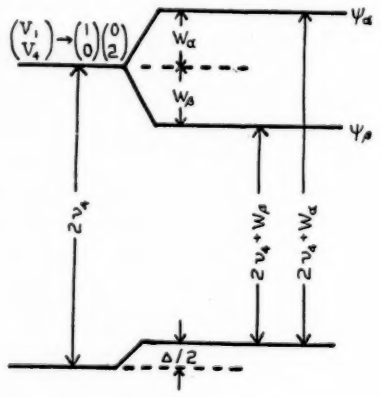

FIG. 1. Resonance splitting of energy levels.

$W_\alpha=\Delta+[\Delta^2/4+b^2/2]^{\frac{1}{2}}$

$W_\beta=\Delta-[\Delta^2/4+b^2/2]^{\frac{1}{2}}$

$\psi_\alpha\sim[\Delta/2-W_\alpha]\psi_\sigma^{V_1=1}\psi_\rho^{V_4=0}+(b/2^{\frac{1}{2}})\psi_\sigma^{V_1=0}\psi_\rho^{V_4=2}$

$\psi_\beta\sim(b/2^{\frac{1}{2}})\psi_\sigma^{V_1=1}\psi_\rho^{V_4=0}+[3\Delta/2-W_\beta]\psi_\sigma^{V_1=0}\psi_\rho^{V_4=2}$.

[3] Adel and Dennison, Phys. Rev. **43**, 716 (1933); **44**, 99 (1933).

centers (ν_1, $2\nu_4$), or the mean of the two corresponding Raman lines for the gas; and where Λ is the interval between the two band centers.

Employing the data given in the first part of Table I, we find the values for Δ and $|b|$ which

TABLE I. *Infrared and Raman spectra of methyl halides.* Infrared band centers[4] in *italics*, for gaseous absorption. Raman lines[5] for scattering by liquids.

		CH_3I	CH_3Br	CH_3Cl	CH_3F
A	ν_5	*534*	*610*	*734*	*1049*
		522	594	712	
B	ν_6	*885*	*957*	*1020*	*1200*
C	ν_3	*1252*	*1305*	*1355*	*1476*
		1239	1296	1357	1462
D	ν_4	*1445*	*1450*	*1460*	*1476*
		1416			
E	(ν_1, $2\nu_4$)	*2855*	*2861*	*2880*	*2862*
		2889		2815	
F	(ν_1, $2\nu_4$)	*2971*	*2972*	*2967*	*2965*
		2947	2956	2955	
G	ν_2	*3074*	*3061*	*3047*	*2987*
		3046	3050	3024	
Δ in cm^{-1}		23	16	4	−38
$\lvert b\rvert$ in cm^{-1}		80	78	62	68
($3\nu_4$, $\nu_1+\nu_4$) predicted		4286	4288	4322	4322
		4440	4444	4446	4458

are tabulated in the second part of Table I. These values are in a class with those found for the carbon dioxide molecule, and it is thus apparent that a precise correlation of the infrared and Raman data for the methyl halide molecules will demand a treatment similar to the one accorded CO_2; namely, an analysis based upon the resonance interaction. An extended calculation of this type must be projected for the future when there will be more data available on the harmonic and combination bands in these spectra. The foregoing analysis can be employed to compute the expected positions of these bands correct to the first order; for example, the pair of bands ($3\nu_4$, $\nu_1+\nu_4$) may be expected at approximately the positions listed in the last line of Table I.

Raman data are available for many other methyl compounds and the pair of lines corresponding to bands E and F occur quite generally. However, because of the lack of observations in the infrared, ν_4 cannot always be determined. Table II indicates a few more examples.

TABLE II.

	ν_4	(ν_1, $2\nu_4$)	
CH_3OH	—	2835	2943
CH_3SH	—	2871	2972
CH_3C_2H[6]	—	2871	2928
C_2H_6	1460	2890	2950
C_6H_{14}	1455	2862	2941
C_8H_{18}	1448	2870	2934

There is also an indication of resonance in CH_4, but here the band D (now designated ν_2) is inactive both for infrared and Raman excitation, and cannot be located directly. With Dennison's value, $\nu_2 \leqq 1520$ cm^{-1},[7] and the observed Raman lines at 2915 and 3072 as (ν_1, $2\nu_2$), we find for methane

$$\Delta = \bar{R} - 2\nu_2 = \tfrac{1}{2}(2915+3072) - 2\times 1520 = -46 \text{ cm}^{-1};$$

$$|b| = +[(\Lambda^2-\Delta^2)/2]^{\frac{1}{2}} = +(22{,}533/2)^{\frac{1}{2}} = 107 \text{ cm}^{-1}.$$

The large value of Δ is significant. It shows that the resonance interaction is weak, and thereby accounts for the observation that the 3072 cm^{-1} Raman line is but one-tenth as strong as the one at 2915 cm^{-1}. The weakness of this interaction is also indicated by observations on the combination bands of methane. Several bands are known which involve ν_1, but none involving $2\nu_2$ have been observed.[8]

[4] Infrared measurements from (1) and from Barker and Plyler (to be published).
[5] Raman data from Kohlrausch, *Der Smekal-Raman-Effekt*, where original references may be found.
[6] Glockler and Davis, Phys. Rev. **41**, 370 (1932).
[7] Dennison, Astrophys. J. **62**, 84 (1925).
[8] Adel and Slipher, Phys. Rev. **46**, 240 (1934).

The Normal Frequencies of Vibration of Symmetrical Pyramidal Molecules AB_3 with Application to the Raman Spectra of Trihalides*

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The symmetrical pyramidal molecule AB_3 is treated by a general normal-coordinate method, six force constants being required. The convenience of the use of "symmetry coordinates" is illustrated in obtaining the formulas for the normal frequencies for several types of potential functions. It is found that with two constants the central force treatment and valence force treatments fit the data equally well. The four constants K, H, K' and H' of the potential function

$$2V = K\Sigma_i \Delta R_i^2 + \tfrac{1}{2}HR_0^2\Sigma_{ij}'\Delta\alpha_{ij}^2 + K'\Sigma_{ij}'\Delta R_i\Delta R_j + 2H'R_0^2(\Delta\alpha_{12}\Delta\alpha_{23} + \Delta\alpha_{23}\Delta\alpha_{31} + \Delta\alpha_{31}\Delta\alpha_{12})$$

for certain trihalides are obtained from Raman data. The interatomic distances calculated using these values of K in the empirical relation found by Badger for diatomic molecules agree with the distances obtained by other methods to within about 0.1A.

THE normal coordinate treatment for symmetrical pyramidal molecules of the type AB_3 has been carried out by Dennison,[1] using central forces, and by Lechner,[2] using valence forces, both treatments involving two force constants. The latter formulas have not previously been applied to any actual molecules. We have treated this problem from a general viewpoint and have then considered several valence-type approximate potential functions. In order to obtain a set of force constants which might be of use in the interpretation of the spectra of more complicated molecules we have applied one of these treatments, involving four force constants, to the observed spectra of trihalides.

Symmetry Considerations

Table I summarizes the facts which may be obtained from the symmetry of the molecule concerning the normal modes of vibration. The numbers under E, $2C_3$, $3\sigma_v$ are the characters of the normal modes corresponding to the operations identity (E), rotation by $\pm 2\pi/3(2C_3)$, and reflection through the planes of symmetry ($3\sigma_v$).

TABLE I. *Characters for the normal modes of vibration (Point group C_{3v}).*

	E	$2C_3$	$3\sigma_v$	Number of modes
A_1	1	1	1	2
E_1	2	−1	0	4

The symbols A_1 and E_1 refer to the two types of normal modes which occur in this molecule. The last column gives the number of modes belonging to each symmetry type. Two normal modes of vibration occur in the symmetry type A_1, each of which is completely symmetric and non-degenerate. There are two pairs of modes in the class E_1, the two members of each pair having the same frequency and being related to each other by rotation about the threefold axis in the manner shown by the characters of Table I.[3] The four fundamental frequencies are allowed in both the Raman and infrared spectra. Table II gives

TABLE II. *Degeneracy, symmetry type, depolarization of Raman lines, and infrared rotational band character for the four fundamental frequencies.*

	Deg.	Sym.	Depol.	Band type
ν_1	1	A_1	$<\frac{3}{4}$	∥
ν_2	1	A_1	$<\frac{3}{4}$	∥
ν_3	2	E_1	$\frac{3}{4}$	⊥
ν_4	2	E_1	$\frac{3}{4}$	⊥

further information concerning their properties.

The symmetry also enables us to factor the secular equation into three quadratic factors, two of which are identical. In order to carry out this factorization, it is only necessary to express the potential and kinetic energies in terms of the

* Contribution No. 424.

[1] D. M. Dennison, Phil. Mag. **1**, 195 (1926).

[2] F. Lechner, Wien. Bericht **141**, 633 (1932).

[3] These results, which are of course well known for this molecule, are best obtained by the group-theory methods of Wigner, Gött. Nachrichten, p. 133 (1930). For other discussions of this method see L. Tisza, Zeits. f. Physik **82**, 48 (1933); G. Placzek, *Rayleigh-Streuung und Raman Effeckt*, Leipzig, 1934; R. S. Mulliken, Phys. Rev. **43**, 279 (1933); E. Bright Wilson, Jr., Phys. Rev. **45**, 706 (1934).

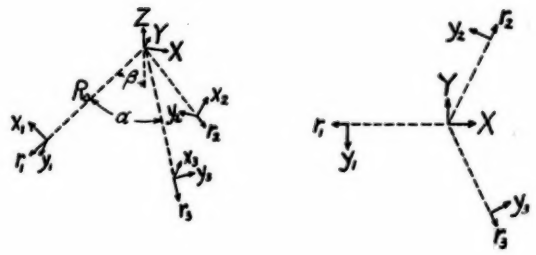

FIG. 1. Perspective view and projection on plane B_3 of coordinate system for molecule AB_3. r_i points along $A-B_i$. x_i lies in plane formed by axis and bond AB_i. y_i is perpendicular to this plane.

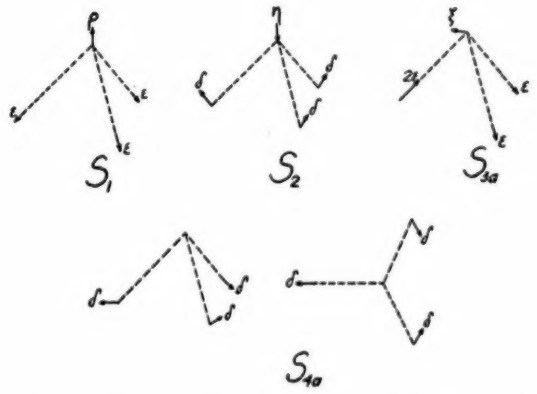

FIG. 2. Graphical representation of symmetry coordinates. In S_{4a} the B atoms all move in plane B_3 in the manner shown by the projection on this plane. $\rho=3\epsilon(m/M)\cos\beta$; $\eta=3\delta(m/M)\sin\beta$, $\xi=3\epsilon(m/M)\sin\beta$.

proper kind of coordinates. We shall for convenience call such a set of coordinates, which factors the secular equation to the maximum extent possible from symmetry considerations alone, a set of *symmetry coordinates*. There will usually be an infinite number of such coordinate sets possible; convenience dictates which one to choose. The symmetry coordinates we have used for this molecule are represented graphically in Fig. 2, the component along a given coordinate direction q_i of the arrow attached to the related atom being the coefficient of the corresponding symmetry coordinate S_k in the transformation for q_i,

$$q_i=\Sigma_{(k)}s_{ik}S_k, \tag{1}$$

in which q_i is one of the original coordinates, such as r_1, shown in Fig. 1.

The criteria by which these coordinates are constructed are as follows: Each symmetry coordinate must belong to one of the symmetry types (irreducible representations) allowed for the modes of vibration; i.e., it must transform in one of the ways given in Table I. There must be as many independent symmetry coordinates of each type as there are modes of vibration of that type. Each symmetry coordinate indicates a motion which conserves angular and linear momentum. The symmetry coordinates corresponding to degenerate symmetry types are constructed so that the members of a given degenerate pair are mutually orthogonal. With these rules it is usually not difficult to construct a set of symmetry coordinates. In the present case it is evident from Fig. 2 that S_1 and S_2 are both completely symmetric as required of the two symmetry coordinates associated with A_1 while it is easy to show that S_{3a}, S_{3b}, S_{4a} and S_{4b} transform as required for type E_1. It is also evident from inspection of the figure that they all conserve momentum.

CALCULATION OF FREQUENCIES FROM SYMMETRY COORDINATES

It can be shown that a set of coordinates which satisfies the above conditions will make it possible to express the potential and kinetic energies (assuming, of course, a homogeneous, quadratic potential function) as quadratic functions of the S's and $\dot{S}$'s without the appearance of any cross terms except between S's or $\dot{S}$'s of the same symmetry type. Thus, in our case, the expressions are

$$2V=a_{11}S_1^2+2a_{12}S_1S_2+a_{22}S_2^2+a_{33}(S_{3a}^2+S_{3b}^2)+2a_{34}(S_{3a}S_{4a}+S_{3b}S_{4b})+a_{44}(S_{4a}^2+S_{4b}^2) \tag{2}$$

and

$$2T=b_{11}\dot{S}_1^2+2b_{12}\dot{S}_1\dot{S}_2+b_{22}\dot{S}_2^2+b_{33}(\dot{S}_{3a}^2+\dot{S}_{3b}^2)+2b_{34}(\dot{S}_{3a}\dot{S}_{4a}+\dot{S}_{3b}\dot{S}_{4b})+b_{44}(\dot{S}_{4a}^2+\dot{S}_{4b}^2). \tag{3}$$

For this molecule the most general quadratic potential function compatible with the symmetry of the molecule has thus only six independent constants.[4] Using the coordinates S, we may set

[4] This simple method of finding the number of independent constants in the quadratic potential function for a molecule of a given symmetry is generally applicable. The group theory considerations, which are very easy to apply, give directly the number and degrees of the factors of the secular equation. For each distinct linear factor there will

up the equations of motion and solve them in the usual manner, obtaining a secular determinant which, when factored, leads to the equations

$$\begin{vmatrix} a_{11}-b_{11}\lambda & a_{12}-b_{12}\lambda \\ a_{12}-b_{12}\lambda & a_{22}-b_{22}\lambda \end{vmatrix}=0$$

and

$$\begin{vmatrix} a_{33}-b_{33}\lambda & a_{34}-b_{34}\lambda \\ a_{34}-b_{31}\lambda & a_{44}-b_{44}\lambda \end{vmatrix}=0, \quad (4)$$

the second factor occurring twice. $\lambda=4\pi^2\nu^2$. ν_1 and ν_2 are the roots of the first equation, while ν_3 and ν_4 are the roots of the second.

The constants b_{ij} depend on the symmetry coordinates selected, the masses of the atoms, and the geometry of the molecule. In our case we obtain

$$2T=3m\{N\dot{S}_1^2+2P\dot{S}_1\dot{S}_2+C\dot{S}_2^2 +(C+1)(\dot{S}_{3a}^2+\dot{S}_{3b}^2)-2\mu(\dot{S}_{3a}\dot{S}_{4a}+\dot{S}_{3b}\dot{S}_{4b}) +(\dot{S}_{4a}^2+\dot{S}_{4b}^2)\}, \quad (5)$$

so that

$$\begin{aligned} &b_{11}=3mN, && b_{12}=3mP, && b_{22}=3mC, \\ &b_{33}=3m(C+1), && b_{34}=-3m\mu, && b_{44}=3m, \end{aligned} \quad (6)$$

with $N=(3m/M)\cos^2\beta+1$, $C=(3m/M)\sin^2\beta+1$, $P=-(3m/M)\sin\beta\cos\beta$, $\mu=\sin\beta$. M and m are the masses of A and B, respectively, while β is the angle shown in Fig. 1.

The constants a_{ij} of the potential energy are what we are seeking to find by using the observed spectra. Since, however, there are only four fundamentals, we cannot evaluate the six independent force constants and it is necessary to make some physical assumptions.[5]

Potential Energy Function

One type of physical assumption which has been used to reduce the number of force constants is the assumption of central forces used by Dennison.[1] His potential function is

$$2V=K_1(\Delta R_1^2+\Delta R_2^2+\Delta R_3^2) +K_2(\Delta r_{12}^2+\Delta r_{13}^2+\Delta r_{23}^2), \quad (7)$$

in which ΔR_i is the change in the distance $A-B_i$ while Δr_{ij} is the change in distance B_i-B_j. K_1 and K_2 are the force constants. This is easily expressed in terms of the coordinates S by using Fig. 2, and by inspection expressions for the a_{ij} are determined. Substitution of these in Eq. (4) gives Dennison's results.

If, on the other hand, we assume that there are no direct forces acting between the non-bonded atoms but that the atoms are held in place by the rigidity, both lateral and extentional, of the chemical bonds, we might assume that a reasonable form for the potential function is

$$2V=K(\Delta R_1^2+\Delta R_2^2+\Delta R_3^2) +HR_0^2(\Delta\alpha_{12}^2+\Delta\alpha_{13}^2+\Delta\alpha_{23}^2), \quad (8)$$

in which α_{ij} is the angle B_i-A-B_j and R_0 the distance $A-B$ at equilibrium. K and H are the force constants. By writing this in terms of the symmetry coordinates S, we get expressions for the a_{ij}'s from which we may obtain Lechner's[2] results.

A more extreme valence type of potential function is obtained from a consideration of Pauling's ideas concerning the chemical bond.[6] From this viewpoint, the stability of a molecule is due to the overlapping of the bond eigenfunctions of the bonded atoms. In our example the central atom A is assumed to have three eigenfunctions whose directions of maximum value are the bond directions. We shall assume that these retain their relative positions but that when the molecule is distorted from the equilibrium position in any manner the whole figure formed by these eigenfunctions rotates until the overlapping with the eigenfunctions from the B atoms is as large as possible, thus giving the molecule the lowest energy for that configuration of the atoms. The potential function corresponding to this picture of the molecule is

$$2V=K(\Delta R_1^2+\Delta R_2^2+\Delta R_3^2) +HR_0^2(\Delta\sigma_1^2+\Delta\sigma_2^2+\Delta\sigma_3^2), \quad (9)$$

be one, for each distinct quadratic factor three, for each distinct cubic six, and in general for each distinct factor of the k'th degree there will be $k(k+1)/2$ independent constants in the most general quadratic potential function for the molecule. One of us (E. Bright Wilson, Jr., J. Chem. Phys. **2**, 432 (1934)) has given tables summarizing the results of group-theory considerations as applied to a large class of molecules. The numbers in the last column of Tables I–VII of this paper give the degrees of the factors of the secular equation so that these tables may be used as indicated above to find the number of independent force constants.

[5] The use of isotopic molecules theoretically gives more data with which to calculate the six force constants, but practically the shifts are so small for all but the hydrogen isotope that they are not of much use.

[6] Linus Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

where $\Delta\sigma_i$ is the angle between the direction of the maximum of the bond eigenfunction for the atom A and the direction of the line $A-B_i$. The mutual directions of the three bond eigenfunctions are kept fixed but their absolute orientation relative to the B atoms is varied until for each configuration of the molecule $\Delta\sigma_1^2+\Delta\sigma_2^2+\Delta\sigma_3^2$ is a minimum. This potential function leads to the equations

$$\begin{aligned} &m^2\lambda^2-[KN+HC]m\lambda+KH\gamma=0,\\ &m^2\lambda^2-[\tfrac{1}{2}K(C+1)+HGW]m\lambda+KHGD=0, \end{aligned} \tag{10}$$

in which N and C have been given above with Eq. (6), and

$$\gamma=3m/M+1,\quad G=(8-7\sin^2\beta)/(4-3\sin^2\beta)^2,$$
$$W=((3m/2M)\sin^2\beta-1)\sin^2\beta+2,$$
$$D=(3m/M-1)\sin^2\beta+2.$$

Finally we have considered a potential function of the type used by Lechner with the addition of two more constants, which we have chosen in the following way

$$\begin{aligned} 2V=&K(\Delta R_1^2+\Delta R_2^2+\Delta R_3^2)\\ &+HR_0^2(\Delta\alpha_{12}^2+\Delta\alpha_{23}^2+\Delta\alpha_{13}^2)\\ &+2K'(\Delta R_1\Delta R_2+\Delta R_2\Delta R_3+\Delta R_3\Delta R_1)\\ &+2H'R_0^2(\Delta\alpha_{12}\Delta\alpha_{23}+\Delta\alpha_{23}\Delta\alpha_{31}+\Delta\alpha_{12}\Delta\alpha_{31}). \end{aligned} \tag{11}$$

This function would be the general one if we had included two more constants, the interaction of the stretching of each bond with the change of the adjacent angles, and the interaction of the stretching of each bond with the change of the angle opposite. We were guided in deciding to neglect these two rather than any other pair by the discussion which Van Vleck and Cross[7] have made of the water molecule in which they decided that the interaction of stretching and bending is the least important. With these four constants we obtain a set of expressions for the a_{ij} and find that the frequencies are given by the equations

$$\begin{aligned} &m^2\lambda^2-[(K+2K')N+(H+2H')LC]m\lambda\\ &\qquad+(K+2K')(H+2H')L\gamma=0,\\ &m^2\lambda^2-[\tfrac{1}{2}(K-K')(C+1)+(H-H')QW]m\lambda\\ &\qquad+(K-K')(H-H')QD=0, \end{aligned} \tag{12}$$

[7] J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).

in which N, C, γ, W and D have been given above with Eq. (10) while

$$Q=3/(4-3\sin^2\beta)\quad\text{and}\quad L=4\cos^2\beta\cdot Q.$$

Application to Trihalides

These four potential functions have been applied to the observed Raman data for the trihalides of phosphorus, arsenic, antimony and bismuth.[8] The three two-constant potential functions, Eqs. (7), (8) and (9), fit the data with comparable accuracy, as shown by the examples in Table III. Table IV gives the results for the four-constant treatment (Eq. (11)) of these molecules, with which the data can be fitted exactly. The angles for PF_3, $AsCl_3$ and PCl_3 are from electron diffraction studies.[9] The other angles were chosen as reasonable in the light of theoretical considerations and crystal structure evidence.[6] The effect on the force constants of possible inaccuracies in the angles is small compared to the effect due to the inaccuracy of the Raman data.

TABLE III. *Comparison of results of two-constant treatments for PCl_3 and $AsCl_3$.*

		ν obs.	a	b	c
PCl_3	ν_1	510	496 (−14)	466 (−44)	473 (−37)
	ν_2	257	205 (−52)	231 (−26)	243 (−14)
	ν_3	480	497 (+17)	534 (+54)	529 (+49)
	ν_4	190	223 (+33)	219 (+29)	200 (+10)
	$K\cdot10^{-5}$		2.01	2.24	2.24
	$K_2\cdot10^{-5}$		0.867		
	$H\cdot10^{-5}$			0.340	0.565
$AsCl_3$	ν_1	410	426 (+16)	385 (−25)	385 (−25)
	ν_2	193	164 (−29)	183 (−10)	186 (−7)
	ν_3	370	383 (+13)	398 (+28)	398 (+28)
	ν_4	159	174 (+15)	168 (+9)	165 (+6)
	$K\cdot10^{-5}$		1.80	2.10	2.10
	$K_2\cdot10^{-5}$		0.600		
	$H\cdot10^{-5}$			0.234	0.425

Frequencies in cm^{-1} and force constants in dynes/cm, listed under a, b and c, are calculated by the use of the potential function of
(a) Eq. (7) (central forces). $K=K_1$.
(b) Eq. (8) (valence forces).
(c) Eq. (9) (valence forces).

Using the values of K for these molecules we have calculated the interatomic distances R_0 by

[8] Bhagavantam, Ind. J. Phys. **5**, 73 (1930) and Trumpy, Zeits. f. Physik **68**, 675 (1931) have published similar computations for a central force treatment of this type of molecule. They use the angle as a third adjustable parameter and obtain values considerably different from those given by electron diffraction experiments.

[9] We are indebted to Dr. L. O. Brockway for the results for PF_3 and $AsCl_3$.

TABLE IV. *Bond angle α, observed Raman frequencies ν_1, ν_2, ν_3 and ν_4 in cm^{-1}. Calculated force constants K, H, K' and H' in dynes/cm and calculated interatomic distances in Angstroms for trihalides.*

	α	ν_1	ν_2	ν_3	ν_4	$K\times10^{-5}$	$H\times10^{-5}$	$K'\times10^{-5}$	$H'\times10^{-5}$	R_0	R_0-R (obs)
(a) PF_3	100°	890	531	840	486	4.56	1.07	0.39	0.04	1.64	0.09
(b) PCl_3	102°	510	257	480	190	2.11	0.31	0.28	0.06	2.15	0.12
(c) PBr_3	104°	380	162	400	116	1.62	0.27	0.05	0.07	2.31	0.07*
(d) AsF_3	97°	707	341	644	274	3.90	0.40	0.34	0.06	1.80	0.08
(e) $AsCl_3$	96°	410	193	370	159	2.01	0.23	0.19	0.02	2.24	0.03
(f) $SbCl_3$	94°	360	165	320	134	1.75	0.17	0.16	0.02	2.30	−0.10*
(g) $BiCl_3$	93°	288	130	242	96	1.17	0.10	0.15	0.02	2.46	−0.04*

* R(obs) for these molecules taken from Pauling's tables of covalent radii. These values are probably somewhat high for these molecules.
Source of assignments:
(a) D. M. Yost of this laboratory, unpublished results. (b) and (e) See Kohlrausch, *Der Smekal-Raman-Effekt*, p. 201, Julius Springer, Berlin, 1931. (c) Cabannes and Rousset, Ann. de physique **19**, 272 (1933). (d) Yost and Sherborne, J. Chem. Phys. **2**, 125 (1934). (f) Braune and Engelbrecht, Zeits. f. physik. Chemie **B19**, 303 (1932). (g) Bhagavantam, Ind. J. Phys. **5**, 66, 86 (1930).

means of the relation found by Badger[10] connecting the force constant and the interatomic distance in diatomic molecules. The last column of Table IV gives the difference between these values and the distances obtained either from electron diffraction or from Pauling's table of covalent radii.

[10] R. M. Badger, J. Chem. Phys. **2**, 128 (1934).

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A Photographic Method for the Study of Mechanical Models of Vibrating Molecules

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IN the study of the vibrations of complex molecules the mechanical models developed by Kettering, Shutts and Andrews[1] have proved useful as a general aid to the interpretation of spectra and particularly as a means of obtaining suggestions regarding the different possible modes of vibration. One of the chief disadvantages in this method, however, is the difficulty of making certain by means of visual observation just what is taking place when the model vibrates. To overcome this defect a photographic method has been developed for recording the types of motion, as shown in Fig. 1.

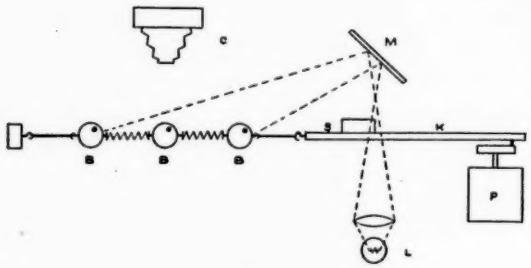

FIG. 1.

White dots, 2 mm diam., are painted with enamel on the balls *B*, *B*, *B* which represent the atoms. A 300 watt lamp *L* is placed so that the greater part of the light from it can be thrown on the model with the help of a mirror *M* and lens. The latter is so arranged that the light beam passes across the reciprocating bar *K* which runs from the motor *P* to the model to transmit the energy of agitation, and is reflected back on the model. It is brought to a rough focus at a point about two centimeters above the bar on which a screen *S* is placed so that at one end of the stroke it cuts down the intensity of the light by 75 percent. The resultant effect is that, when the model is executing a characteristic mode of vibration in phase with the agitating bar, the intensity of the light falling on it at one extreme of the phase is about four times that at the other extreme.

A camera *C* is placed about five feet from the model and arranged so that a time exposure may be taken while the model is vibrating. With

[1] C. F. Kettering, L. W. Shutts and D. H. Andrews, Phys. Rev. **36**, 531 (1930).

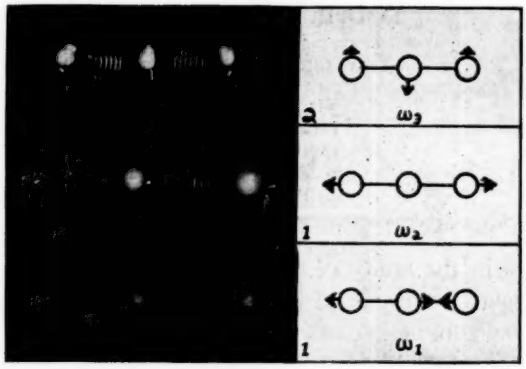

FIG. 2.

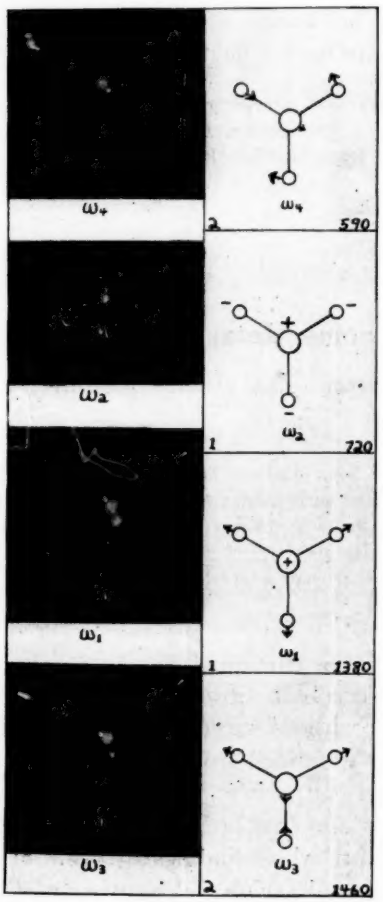

FIG. 3. Vibrations in NH_3.

exposures of about one or two seconds the dots trace out the paths over which the atoms are vibrating, the intensities at the ends of the paths indicating the phase relations.

Fig. 2 shows the three modes of vibration in a linear triatomic model composed of three balls of equal mass and two springs of equal strength. Fig. 3 illustrates the four modes of vibration in a model of the ammonia molecule. In the case of the degenerate types of vibration, ω_3 and ω_4, only one mode of motion is excited.

The values of the observed frequencies for NH_3 are given in Table I. It seems either that ω_4 does not appear in the Raman spectra as might be expected from Placek's selection rules or that in the molecule the frequencies ω_2 and ω_4 have about the same value. There also appears to be some kind of doublet instead of a simple frequency for ω_3.

The spring was designed to have roughly the ratio of bending to stretching force observed in a number of the C–H vibrations. The numbers given in the left-hand corner opposite each type of vibration indicate the number of degrees of freedom, and in the right hand corner the r.p.m. at which the motion was photographed. The latter have been converted by means of an arbitrary constant (calculated so as to bring ω_1, and the corresponding model frequency* into

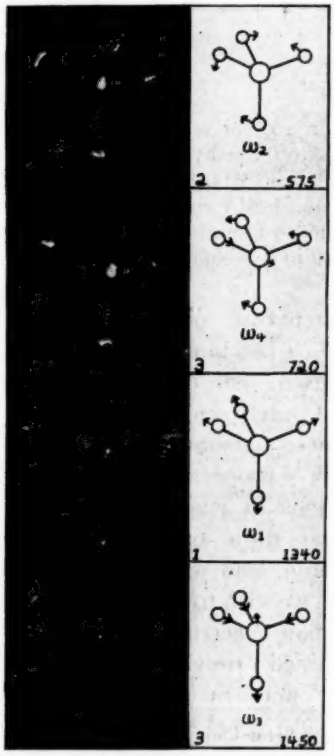

FIG. 4. Vibrations in CH_4.

TABLE I. *Vibrations in NH_3.*

	Raman spectra[2]	Model
ω_1	3210 cm^{-1}	3210*
ω_2	1580	1675
ω_3	3310 }	3400
	3380 }	
ω_4	1580(?)	1370

TABLE II. *Vibrations in CH_4.*

	Spectra[4]	Model
ω_1	2915 cm^{-1}	2915*
ω_2	1304	1260
ω_3	1520	1575
ω_4	3022 }	3180
	3070 }	

agreement) to values comparable with the spectral frequencies. Only the qualitative agreement is significant.

Fig. 4 shows the vibrations observed in CH_4 and the frequencies either observed or deduced from spectra are given in Table II.

The method has been applied with considerable success in the study of some metal carbonyls and alkyls by Duncan and Murray[3] and in the study of the motions of the benzene ring to be discussed in a forthcoming article. It should be especially useful in unsymmetrical compounds such as hydrogen compounds consisting partly of protium and partly of deuterium where the lack of symmetry makes an analytical solution by means of determinants or group theory extremely difficult.

[2] P. Daure, Ann. de physique **12**, 375 (1929).
[3] A. B. F. Duncan and J. W. Murray, J. Chem. Phys. **2**, 636 (1934).
[4] The authors' interpretation of the results of D. M. Dennison, J. Astrophys. **62**, 73 (1925) and Dickinson, Dillon and Rassetti, Phys. Rev. **34**, 582 (1929).

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The Raman and Ultraviolet Absorption Spectra of Some Metal Carbonyls and Alkyls

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The Raman spectra of nickel carbonyl, iron pentacarbonyl, lead tetramethyl, and lead tetraethyl and the ultraviolet absorption spectra of nickel carbonyl, lead tetramethyl and lead tetraethyl have been studied. The symmetry number of nickel carbonyl has been calculated. The vibrations of a mechanical model of a plane XY_4 molecule have been studied. The correlation of the observed Raman lines with modes of vibration is discussed. It is concluded, from the observed spectrum and the vibrations shown by the mechanical model, that nickel carbonyl has a plane rather than a tetrahedral structure.

THE structure of compounds containing metal-carbon homopolar bonds has received little attention. The question is of interest not only from a purely scientific standpoint, but also because these substances are noted for their "anti-knock" properties when used in small concentrations in gasoline. We have obtained new optical data on nickel carbonyl, iron pentacarbonyl, lead tetramethyl and lead tetraethyl which we wish to report here.

The Raman spectrum of nickel carbonyl has been obtained previously by Dadieu and Schneider,[1] and by Anderson.[2] The former authors also attempted to obtain the Raman spectra of cobalt tetracarbonyl and iron pentacarbonyl without success. The lead alkyls have not been examined from this viewpoint heretofore. The ultraviolet absorption spectrum of nickel carbonyl has been examined by Thompson and Garratt[3] whose findings are confirmed by our work. The ultraviolet absorption of the other compounds treated in this work have not been investigated previously.*

[1] Dadieu and Schneider, Anzeiger der Acad. der Wiss. in Wien, Math. Naturwiss. Klasse **68**, 191 (1931).
[2] J. S. Anderson, Nature **130**, 1002 (1932).
[3] H. W. Thompson and A. P. Garratt, J. Chem. Soc. (1934), 524.
* H. W. Thompson (J. Chem. Soc. London, 1934, 790) has recently reported a system of discrete bands belonging to lead tetraethyl which lies on the long wave side of the continuum observed by us and by him. Although we used a slightly longer path and corresponding pressures, we

The modes of vibration of a mechanical model of a plane XY_4 molecule have been investigated in order to facilitate the interpretation of the observed spectra.

Experimental

The Raman spectra of $Ni(CO)_4$, $Pb(CH_3)_4$, and $Pb(C_2H_5)_4$ were obtained with the apparatus described by Murray and Andrews.[4] For iron carbonyl, which is orange colored and decomposes rapidly with light of shorter wave-length than the red, another technique had to be used. The liquids were distilled into the Raman tubes in vacuum by cooling the tubes with solid carbon dioxide, frozen out, and sealed off as they decompose at high temperatures.

The nickel carbonyl was prepared by Mr. C. B. Jackson of this laboratory from carbon monoxide and finely divided nickel. Spectra of this compound were excited by the 4358 and 5461 lines of mercury using a filter of saturated sodium nitrite, nitrobenzene, and praseodymium nitrate solution. The lead tetramethyl was furnished by Professor F. O. Rice and was subjected to vacuum distillation before using. Spectra were excited with the 4358 and 5461 lines as in the case of $Ni(CO)_4$ and also by the 4047 line using a filter of dilute sodium nitrite solution and iodine in carbon tetrachloride. Slight decomposition occurred with the latter method of excitation. The lead tetraethyl was furnished by the Ethyl Gasoline Corporation. The original material, which was quite pure, was fractionated in vacuum before using. It was found to decompose rapidly with violet and blue light. With the green mercury line, decomposition was not noticeable with an eight hour exposure. A filter of copper nitrate, didymium nitrate, and potassium chromate was used to obtain monochromatic green light. Several exposures were obtained with the filter used for blue excitation but the irradiation was limited to 20 minutes with one arc by decomposition and the appearance of a white precipitate. The iron carbonyl was obtained from the General Motors Corporation in the form of a 50 percent solution in kerosene. The iron carbonyl was separated by distillation in an atmosphere of nitrogen in red light as preliminary experiments had shown that it decomposes rapidly in green light with the formation of orange crystals. The spectrum was excited by the 6439 line of cadmium. The source of illumination was a cadmium-tin quartz arc as recommended by Krishnamurti.[5] The arc was about 12 cm long with electrodes of tungsten wire sealed in with picein and cooled by water jackets. The arc was operated in the vertical position on a current of 6 amperes with continuous pumping. It was surrounded by a semi-elliptical reflector and cooled by an air jet. The Raman tube was placed in the vertical position and had its window sealed onto a smaller tube projecting into the liquid at the top in order to keep the window free from the crystals formed by decomposition. The Raman tube was surrounded by a filter jacket containing a filter of iodine and potassium iodide dissolved in water and the tube and jacket were cooled in running water. This arrangement permitted intense illumination with the cadmium red line while no lines of wave-length (less than 6300) were recorded on the plate with a 65 hour exposure. The spectrum was photographed on Eastman Spectroscopic plates, I–F and I–N which have adjacent bands of maximum sensitivity covering the spectral region between the cadmium red line and 8000A which includes all of the Raman lines to be expected for this type of substance. The plates were hypersensitized with ammonia just before using.

The apparatus used for investigating the polarization of the Raman lines of nickel carbonyl and lead tetramethyl differed from those described in the literature in a few details and will be discussed briefly. Strictly quantitative data were not necessary for our purpose so several simplifications could be made. The illumination was furnished by a quartz capillary arc focussed by reflectors. The illumination was perpendicular to the direction of observation and to the spectrograph slit and was restricted to an angle of five degrees from the principal direction by a set of parallel strips of blackened cardboard set in planes perpendicular to the axis of the Raman tube. The Raman tube was in a vertical position and the light emerging from the window at the

obtained no evidence of them. We must conclude that our dispersion and resolving power were too low (Hilger E 37 used).

[4] J. W. Murray and D. H. Andrews, J. Chem. Phys. **1**, 406 (1933).

[5] P. Krishnamurti, Ind. J. Phys. **5**, 587 (1930).

TABLE I. *Nickel carbonyl.*

$\bar{\nu}$	$\Delta\bar{\nu}$	Ex.	I	P	ν	$\Delta\bar{\nu}$	Ex.	I	P	$\bar{\nu}$	$\Delta\bar{\nu}$	Ex.	I	P
23532	−594	*h*	0		22396	599	*g*	1		20953	2042	*g*	4	
23396	−458	*h*	3		22337	601	*h*	4		20895	2043	*h*	30	*p*
23314	−376	*h*	10	*P*	22220	718	*h*	0		20806	2132	*h*	5	
22856	82	*h*	100	*p*	22105	833	*h*	2		20715	2223	*h*	1	
22658	381	*f*	2		22066	872	*h*	2		18230	78	*k*	100	*p*
22613	382	*g*	4		22025	913	*h*	2		17922	386	*k*	20	*P*
22556	382	*h*	20	*P*	21329	1609	*h*	0		17840	464	*k*	8	
22475	463	*h*	8	*D*	21001	2038	*f*	2						

82(100, *p*), 382(20, *P*), 463(8, *D*), 601(4), 718(0), 833(2), 872(2), 913(2), 1609(0), 2043(30, *p*), 2132(5), 2223(1).

TABLE II. *Lead tetramethyl.*

$\bar{\nu}$	$\Delta\bar{\nu}$	Ex.	I	P	$\bar{\nu}$	$\Delta\nu$	Ex.	I	P	ν	$\Delta\bar{\nu}$	Ex.	I	P
24235	470	*d*	3*b*		22463	475	*h*	20	*D*	21517	2999	*e*	7	
24054	462	*e*	0		22413	2292	*d*	1		21418	2917	ν_3	1	
23543	1162	*d*	4		22361	577	*h*	0		21026	3679	*d*	1*b*	
23531	1174	*d*	4		22171	767	*h*	1		20950	3755	*d*	1*b*	
23455	−460	*g*	0		22008	930	*h*	0		20022	2916	*h*	5	*P*
23410	−472	*h*	2		21882	1157	*f*	1		19945	2993	*h*	1	
23398	−460	*h*	5		21829	1166	*g*	4		18444	−136	*k*	8	*D*
23343	1173	*e*	1		21786	2919	*d*	50		18182	126	*k*	20	*D*
22804	134	*h*	80*b*	*D*	21783	1155	*h*	20	*D*	17840	468	*k*	10	*p*
22572	467	*f*	4	*p*	21768	1170	*h*	10	*p*	17161	1147	*k*	2	
22529	466	*g*	10	*p*	21705	3000	*d*	30		17147	1161	*k*	1	
22478	460	*h*	100	*p*	21597	2919	*e*	10						

130(80, *D*), 460(100, *p*), 473(20, *D*), 577(0), 767(1), 930(0), 1155(20, *D*), 1170(10, *p*), 2292(1), 2918(50, *P*), 2999(30), 3679(1), 3755(1).

TABLE III. *Lead tetraethyl.*

$\bar{\nu}$	$\Delta\bar{\nu}$	Ex.	I	$\bar{\nu}$	$\Delta\bar{\nu}$	Ex.	I	$\bar{\nu}$	$\Delta\bar{\nu}$	Ex.	I
23377	−439	*h*	1	20072	2866	*h*	1	17839	469	*k*	5
22696	242	*h*	2	20022	2916	*h*	2	17773	535	*k*	1
22496	442	*h*	10	18751	−443	*k*	1	17299	1009	*k*	2
22476	462	*h*	5	18549	−241	*k*	1	17155	1153	*k*	5
21924	1014	*h*	2	(18212)	96	*k*	10*b*	16848	1460	*k*	1
21775	1163	*h*	5	18069	239	*k*	2	15436	2872	*k*	1
21479	1459	*h*	1	17862	446	*k*	10	15381	2927	*k*	5

(96(20*bb*)), 241(2), 443(10), 464(5), 535(1), 1012(2), 1159(5), 1460(1), 2869(1), 2927(5).

bottom was reflected to the spectrograph by a right-angled prism. It was focussed on the slit by a lens of 18 cm focal length and passed through a Wollaston prism. This apparatus gave satisfactory results in a check experiment with carbon tetrachloride, the polarization of whose Raman lines is well known.

The technique for the study of the mechanical model of the plane XY_4 molecule was the same as that described by Andrews *et al.*[6]

[6] D. H. Andrews and J. W. Murray, J. Chem. Phys. **2**, 634 (1934).

RESULTS

The results obtained on the Raman spectra of $Ni(CO)_4$, $Pb(CH_3)_4$, and $Pb(C_2H_5)_4$ are presented in Tables I to III. The first column gives the wave numbers of observed Raman lines in cm^{-1}, the second column, the displacement from the exciting line or Raman frequency, the third column, the mercury line which excited the Raman line, the fourth column, the relative intensity, and the fifth column, the state of polarization, if determined. The accuracy of the wave number values is believed to be about 3

cm^{-1} for lines of average intensity and sharpness. The symbols used for the mercury lines are: *d* 24,705 cm^{-1}, *e* 24,516, ν_3 24,335, *f* 23,039, *g* 22,995, *h* 22,938 and *k* 18,308. The reported intensities are estimated visually, series of graded exposures being used for the stronger lines. The symbols for the state of polarization are: *P*, strongly polarized; *D*, largely depolarized; and *p*, intermediate. The results for $Ni(CO)_4$ are taken from four plates with blue and green excitation, those for $Pb(CH_3)_4$ from four plates with blue and green excitation and two with violet excitation, and those for $Pb(C_2H_5)_4$ are taken from two plates with green excitation and one with blue excitation. In the case of the iron pentacarbonyl, the plates taken on I–N spectroscopic plates showed no Raman lines even with an exposure of 65 hours. In exposures of this length, crystals of the orange decomposition product formed in the tube even with red light and hence the cadmium spectrum was very strong due to the reflected light. With a I–F plate, two faint diffuse lines were observed at 15,211 and 15,033 cm^{-1} which correspond to displacements of 320 and 498 cm^{-1}, respectively. Due to the low intensity of these lines and the presence of considerable fog on the plate which was hypersensitized in ammonia, these lines must be regarded as of doubtful authenticity.

The motions observed in the mechanical model of the plane XY_4 molecule are represented in Fig. 1 by photographs and drawings together with the number of degrees of freedom corresponding to each motion, a number designating the type of motion, its frequency relative to that of ω_1 set equal to the Raman frequency assigned to it, and the frequencies of the Raman lines assigned to these motions. This method of investigating the vibrations of molecules has several limitations which must be considered in interpreting the results. The actual values of the observed frequencies have no significance and hence are not given here. The motions observed may be distorted by the effects of the angular moments of inertia of the balls representing the atoms, the mass of the spring, resistance to rotation around the bond, and inequalities in the masses of the balls and springs and the force constants of the springs. The photographs show the directions and amplitudes of the motions of the balls by the traces of white dots painted on the balls. The phase relations are indicated by cutting off the light at one end of the vibration. Rotation of the balls caused slight variations in the apparent directions of the ball motions, especially in ω_1 and ω_7.

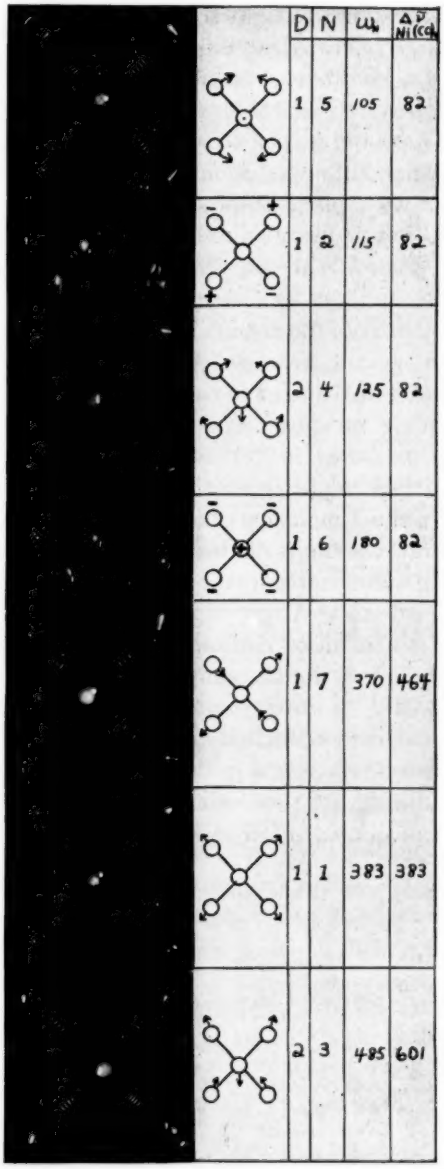

FIG. 1.

Ultraviolet absorption spectra

The absorption spectra of the vapors of nickel carbonyl, lead tatramethyl and lead tetraethyl were photographed with a small Hilger quartz

spectrograph. The light source was an hydrogen discharge operated at 0.05 ampere and 10,000 volts a.c. Hydrogen from a palladium tube flowed through the discharge during the exposures and the continuum was entirely free from bands. The absorption tube was about 30 cm long, of fused quartz with plane ends sealed on. The liquids were contained in a small bulb joined to the tube by a graded seal and the pressure in the absorbing column was adjusted by varying the temperature of the liquid.

The spectra were perfectly continuous at all pressures tried and gave no indication of bands at the lowest pressures. It is possible that, at still lower pressures in correspondingly longer columns, these might appear but it seems unlikely in view of the complexity of the molecules. We give, therefore, the limits of absorption observed at the corresponding temperatures of the liquid or solid in the side tube. Vapor pressures are known only in the case of nickel carbonyl. The exact measurement of the limits seemed unnecessary. The results are of interest in the possible photochemical decomposition of these substances in the gaseous state, and in the reactions which may be induced by the radicals formed by these decompositions, at low temperatures. (Table IV.)

TABLE IV.

Compound	Temperature	Limits of absorption
$Ni(CO)_4$	−78°C (p=0.7 mm)	All light absorbed below 3350
	25°C (p=398 mm)	3600
$Pb(CH_3)_4$	−78	no absorption
	−25	2650
	0	2700
	25	2750
$Pb(C_2H_5)_4$	−78 pressure very low	2300
	25 pressure very low	2550

DISCUSSION

As the molecules under consideration show great dissimilarities in their spectra and are rather different mechanically, it appears best to discuss each compound separately.

Nickel carbonyl

The results obtained for this substance confirm all of the lines reported by previous investigators. New lines have been found at: 718, 833, 872, 1609 and 2223 cm^{-1}.

The structure of this molecule has been considered to be a ring in which the nickel atom is joined to only two carbon atoms.[7, 8] Sutton and Bentley[9] have determined the dipole moment of nickel carbonyl and find it to be very low, probably zero, which indicates a high degree of symmetry more in accord with a plane square or a tetrahedral structure than with a ring. Blanchard and Gilliland[10] proposed an electronic configuration in which each of the CO groups shared two pairs of electrons with the central nickel atom. Pauling[11] suggests that four nickel-carbon bonds are present and are directed toward the corners of a square, all lying in one plane.

Dadieu and Schneider[1] assumed that the structure was tetrahedral and interpreted their results on that basis, assigning to ω_1 463, ω_2 82, ω_3 601, and to ω_4 382. 913 was assigned to the harmonic of ω_1 and the higher frequencies were assigned to the stretching motions of the CO bonds. These authors, as well as Anderson,[2] pointed out that the proximity of the frequencies of the carbonyl groups to that of the CO molecule indicates that the binding in nickel carbonyl is like that in carbon monoxide rather than like that in the organic carbonyl group. This fact supports the symmetric structures rather than a ring and suggests that the Ni−CO bond is formed by a single pair of electrons.

Consideration of the more complete Raman data now available, which include measurements of the polarization of the lines, indicates that the assignments made by Dadieu and Schneider are incorrect and that the molecule is probably plane as suggested by Pauling. This conclusion is supported by a calculation of the symmetry number. Nickel carbonyl should have 21 vibrational degrees of freedom. In view of the fact that the frequencies of vibration of the CO bond are much higher than those for the motions of the Ni−CO bonds, we may consider the molecule as a pentatomic molecule with nine degrees of freedom for the vibrations of low frequency. The

[7] J. W. Mellor, *A Comprehensive Treatise of Inorganic and Theoretical Chemistry*, Vol. 5, p. 954.
[8] Sugden, *The Parachor and Valency*, p. 189.
[9] Sutton and Bentley, Nature **130**, 314 (1933).
[10] A. A. Blanchard, and Gilliland, J. Am. Chem. Soc. **48**, 872 (1926).
[11] L. Pauling, J. Am. Chem. Soc. **53**, 1398 (1931).

remaining 12 are associated with the internal motions of the CO groups and motions involving partial rotations of the CO groups about axes perpendicular to the Ni−CO bond axes, or twisting motions. The lines at 2043, 2132 and 2223 are associated with the internal motions, the lowest value being assigned to the symmetrical type on account of its polarization and intensity.

If the tetrahedral pentatomic structure is considered, we should expect the 9 degrees of freedom to be divided among four motions: a nondegenerate symmetrical stretching motion, ω_1; a doubly degenerate bending motion in which two pairs of Ni−CO bonds bend in scissor fashion, ω_2; a triply degenerate unsymmetrical stretching motion, ω_3; and a triply degenerate unsymmetrical bending motion, ω_4; as in the case of carbon tetrachlorode.

ω_1 must be assigned to the 382 line on account of the strong polarization. ω_2 must be assigned to the 82 line on account of the low frequency. ω_4 might be assigned to 463 and ω_3 to 601. This would make one bending motion, ω_4, greater that the other, ω_2, by a factor of nearly six and hence this assignment appears very improbable. We may assign both ω_2 and ω_4 to the 82 line as it is very broad, unsymmetrical, and of unusually great intensity which suggests that it is complex. ω_3 would then be assigned to 463 leaving 601, which is fairly intense, unexplained.

If we consider the transition from the tetrahedral structure to a plane square structure, whose motions are shown in Fig. 1, ω_1 remains essentially the same; ω_2 gives two non-degenerate motions, ω_2 and ω_5; ω_3 gives one non-degenerate motion, ω_7, and one doubly degenerate motion, ω_3; and ω_4 gives one non-degenerate motion, ω_6, and one doubly degenerate motion, ω_4. We assign the four bending motions to the broad 82 line, ω_1 to the 382 line, ω_7 to the 463 line, and ω_3 to the 601 line. This permits us to make what appears to be a rational assignment to all of the strong lines in the low region. As seen in Fig. 1, the frequencies observed in the model are in fair agreement with our assignment. As pointed out above, however, this should not carry much weight for the relative stretching and bending constants of the springs may not correspond well to those in the molecule. The separation of ω_1 and ω_7 in the molecular spectrum is explained by the difference in the effects of the repulsion of the CO groups for each other in the two types of motion. This effect is not present in the model so the reversal of the order of the two motions in the spectrum has no significance. It is indeed difficult to see why they should have different frequencies in the model at all.

There remain lines at 718, 833, 872, 913 and 1609 to be explained. Dadieu and Schneider[1] have attributed the 913 line to a harmonic of the 463 line. Some of these lines are probably due to the twisting motions of the CO group but it does not seem probable that such a wide range of frequencies can all be due to this type of motion. The line at 1609 is extremely feeble and is of doubtful origin so no assignment can be made of it at this time. We assign 718, 833, 872 and possibly 913 to this type of motion. In the vibration type ω_1, the central atom is considered to be stationary. If this is the case, the frequency should be that of a diatomic oscillator in which the CO group vibrates against an infinite mass. We have calculated the force constant of the Ni−CO bond on this assumption and obtain the value, 2.4×10^5 dynes per cm which is about the value expected for a single electron pair bond.

The symmetry number of nickel carbonyl

Space will not permit a detailed account of these calculations which were made by the method described by Deitz and Andrews.[12] The vapor pressures were taken from the work of Anderson,[13] and the Raman frequencies observed by us, together with our assignments of degrees of freedom, were used as the basis for the calculation of the necessary thermal data. λ_0 was estimated from the data given in the above work and the difference $\int Cp_{\text{vap.}}dT - \int Cp_{\text{sol.}}dT$. The temperature used was 243°K. The specific heats calculated are shown in Table V. The only value found in the literature[14] is an average over the interval −78 to −188°C and is in fair agreement with our calculations. Preliminary measurements by Dr. S. L. Goldheim and D. Stull in this laboratory have indicated somewhat higher values over the higher part of the temperature range but the method used has not been

[12] V. Deitz and D. H. Andrews, J. Chem. Phys. **1**, 62 (1933).
[13] J. S. Anderson, J. Chem. Soc. **132**, 1653 (1930).
[14] Dewar, Proc. Roy. Soc., London **A89**, 158 (1913).

TABLE V. *The specific heat of nickel carbonyl (solid).*

Temp. °K	Cv (Debye) $\theta=38.2$	$Cp-Cv$	Cv (total)	Cp (solid)
10	6.32	0.003	6.33	6.33
20	10.02	0.179	10.81	10.99
30	11.00	0.312	14.05	14.36
40	11.40	0.45	16.40	16.85
50	11.58	0.58	18.02	18.60
60	11.68	0.71	19.09	19.80
70	11.74	0.83	19.68	20.51
80	11.76	0.96	20.23	21.19
90	11.80	1.07	21.20	22.27
100	11.82	1.21	21.56	22.77
120	11.84	1.47	22.40	23.87
140	11.90	1.72	23.67	25.39
160	11.92	1.96	24.83	26.79
180	11.92	2.20	26.23	28.43
200	11.92	2.44	27.56	30.00
220	11.92	2.73	28.56	31.29
240	11.92	2.94	30.02	32.96

adequately calibrated as yet and considerable decomposition took place so that the results cannot be relied on at this time. The Debye frequency was calculated, as usual, from the melting point formula of Lindemann, the molecular volume of $Co(CO)_4$ being used. The moments of inertia were considered for the two cases of a square and a tetrahedron. Distances were derived independently from several different sources, mainly x-ray measurements on analogous compounds, and no serious differences were found. The values of the product ABC for the cases of the square and the tetrahedron were respectively, 7.62×10^{-112} and 8.84×10^{-112}.

If this molecule has a plane square configuration, the symmetry number should be 8, while if it is tetrahedral, the number should be 12. The value obtained was 6.3 and we believe that, unless some large unknown error is present in the data used, the number would not rise much above this value. This may be taken as some indication that the plane square model is correct or at least more probable than the tetrahedron.

Lead tetramethyl

Since the publication of a recent note,[15] new Raman lines have been found for this compound at 577, 2292, 3679 and 3755, all of which are very weak. The complete data are presented in Table II. We are now able to give a more definite assignment to the lines of this compound which differs, in some respects, from that suggested in our previous note. It appears probable that this compound has a tetrahedral structure although there is no direct evidence on this point from other sources. Lead tetraphenyl has been shown to have this structure by x-ray analysis.[16] By analogy to compounds of other elements in the same group in the periodic system, such a structure should be expected.

On this assumption, we assign ω_2 and ω_4 to the line at 130 which is broad and appears to be double in the microphotometer curves. The 460 line, which is strong and partially polarized, is assigned to ω_1, while the line at 473, which is weaker and largely depolarized is assigned to ω_3. This accounts for the low motions expected in a pentatomic tetrahedral molecule. The line at 930 is attributed to a harmonic of 460 and the line at 2292 to a harmonic of 1155. The lines at 577 and 767, which are very weak, cannot be assigned on the basis of our present ideas. The 767 line is also found in the infrared absorption spectrum which has been examined by Kettering and Sleator.[17] The lines at 1155 and 1170 are assigned to bending motions of the C−H bonds. The line at 2918 is strongly polarized and is assigned to the symmetrical stretching motion of the C−H bonds while the weaker line at 2999 is assigned to an unsymmetrical motion of these bonds. We can offer no good explanation for the weak lines at 3679 and 3755 although they appear on several plates. It seems improbable that they are due to water which has a complex band in this region as they do not coincide with the maxima of this band.

Lead tetraethyl

The experimental data for this compound are probably not as complete as those for lead tetramethyl. This is due to the low dispersion obtained when working in the region of the mercury green line and the difficulties arising from decomposition when working with the blue line. We are confident that a low frequency Raman line of considerable intensity exists. This appears as a broad band not clearly separated from the exciting line and the measurement of its

[15] A. B. F. Duncan, and J. W. Murray, J. Chem. Phys. **2**, 146 (1934).

[16] W. K. George, Proc. Roy. Soc., London **A113**, 585 (1926).

[17] Kettering and Sleator, Physics **4**, 39 (1933).

position is therefore only an approximation.

It may be doubted that a treatment of lead tetraethyl as a pentatomic molecule is completely justified. In view of the apparent similarity of the spectra, however, we have assigned the lower lines on this basis. We should expect deviations from the mechanical behavior of a pentatomic tetrahedral molecule due to the interaction between the internal and twisting motions of the ethyl groups with the motions of the $Pb-(C_2H_5)$ bonds. The data for this compound are given in Table III.

It seems best to assign ω_2 and ω_4 to the broad low frequency line at about 96. By analogy to the case of lead tetramethyl, we assign ω_1 to 443 and ω_3 to 464. The 1012 line is attributed to a stretching motion of the C−C bonds in the ethyl groups. The 1159 line is assigned to a bending motion of the C−H bonds in the methyl groups as it appears in almost exactly the same place in the spectra of lead tetramethyl and the zinc alkyls. The line at 1460 is also attributed to this type of motion as it occupies the position generally attributed to this type of motion. The lines at 2869 and 2927 are attributed to stretching motions of the C−H bonds. No assignment of the line at 241 can be made at this time.

Dadieu and Schneider[1] have stated that nickel carbonyl gave an exceptionally intense Raman spectrum. We have also noticed this in our work. In estimating the relative intensities of the Raman lines, we have made series of short exposures varying the exposure times between one second and 500 or 1000 seconds which permits an approximate measure of the intensity of the Raman line relative to that of the exciting line. The ratio of the intensity of the exciting line to that of the Raman line was found to be between 50 and 100 for the 82 line in $Ni(CO)_4$ and about 100 for the 460 line of lead tetramethyl. A similar experiment with the 992 line of benzene, which is generally considered to be quite intense, gave a ratio of about 200. While the method used yields only a rough approximation and is influenced by the magnitude of displacement of the Raman line from the exciting line, it appears certain that these lines have unusually high intensities. This may be due, in the case of the line of nickel carbonyl, to the superposition of several lines as assumed in our assignment of the frequencies to modes of vibration.

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Absorption of Light in Organic Compounds

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In this paper a first attempt is made to evaluate from published measurements the total strength and width of absorption bands of organic compounds, and to correlate that with the nature of the solvent and the constitution of the substance. It turns out that none of the quantities that one could consider from the theoretical standpoint remains constant.

INTRODUCTION

THE absorption spectrum has long been regarded as closely connected with the molecular structure of organic compounds. Many investigations have been made concerning the influence of substitution and (if, as is mostly the case, the compound is in solution) of the solvent on the wave-length of the absorption maximum, and it has been possible to formulate some general rules. But very little has been done concerning the two other quantities which are characteristic for a continuous absorption band, its width and its strength, and an attempt is made here to supply this deficiency.

THEORY

If a plane wave of frequency ν and wave-length λ in vacuum progresses through an absorbing medium, this can be characterized by a complex refractive index n'

$$n'=n(1-ik), \tag{1}$$

so that the wave amplitude is given by

$$e^{2\pi i\nu(t-n'\,x/c)}=e^{-2\pi nk\,x/\lambda}e^{2\pi i(\nu t-n\,x/\lambda)}.$$

If we have μ mols per liter, the absorption of the light intensity (square of the amplitude) is given by $e^{-\epsilon\mu x}$, where

$$\epsilon=4\pi nk/\lambda. \tag{2}$$

The theory of dispersion shows now that one has

$$n'^2-1=n^2(1-k^2)-1-2n^2ik$$
$$=-\frac{e^2}{\pi m}N'\Sigma\frac{f_j}{\nu_j^2-\nu^2+i\gamma_j\nu}, \tag{3}$$

where the summation on the right is extended over all the absorption bands of frequency ν_j, γ_j is a quantity measuring the damping and responsible for the width of the band, f_j measures the strength. N' is the number of molecules per cc and will be written

$$N'=N\mu \tag{3'}$$

with $N=6.06\times10^{20}$, finally it has been assumed that in the visible and ultraviolet one can put for e and m charge and mass of the electron. f_j, the strength of the band, would in classical theory be the number of electrons per molecule producing that band. In quantum theory, it measures the ratio of the probability of transition for the band to the probability of the standard classical band.[1] The sum of all the f_j is equal to the number of electrons.[2] It has turned out through recent investigations, that most of the characteristic absorption bands, e.g., the ones determining color, are weak bands, while the bands contributing the main part of the refractive index lie in the extreme ultraviolet.

If one considers the neighborhood of one weak absorption band removed from the others, one can write

$$2n^2k=\frac{e^2}{\pi m}N'\frac{\bar{f}_j\gamma_j\nu}{(\nu_j^2-\nu^2)^2+\gamma_j^2\nu^2} \tag{4}$$

and if the band is weak enough, one can neglect the change in n which is contributed by this particular band and write for n the value due to all the other bands at ν.

[1] R. Ladenburg, Zeits. f. Physik **4**, 451 (1921); R. Ladenburg and F. Reiche, Naturwiss. **11**, 584 (1923).

[2] F. Reiche and W. Thomas, Zeits. f. Physik **34**, 510 (1925); W. Kuhn, Zeits. f. Physik **33**, 408 (1925).

We find from (2) and (4)

$$\epsilon=\frac{2e^2}{cm}\frac{N}{n}\frac{\bar{f}_j\gamma_j\nu^2}{(\nu_j^2-\nu^2)^2+\gamma_j^2\nu^2}. \tag{5}$$

If the band is sufficiently narrow, it follows

$$\int\epsilon d\nu=\frac{\pi e^2}{cm\nu_j^2}\frac{N}{n}\bar{f}_j \tag{6}$$

independent of γ.

Similarly, Fuchtbauer[3] has shown that from the quantum standpoint one should get the integral on the left side of (6) to be proportional to the probability of transition, and for a gas $n=1$ one gets then

$$\int\epsilon d\nu=\frac{\pi e^2}{cm\nu_j^2}Nf_j. \tag{6'}$$

While this f cannot be interpreted as "electron number" for $n\neq1$, it is also listed in the tables.

A closer inspection of his reasoning shows that this should be replaced for a broad band by

$$\int\epsilon\nu d\nu=(\pi e^2/cm\nu_j)Nf_j, \tag{6''}$$

but numerically there is only a small difference between (6') and (6'') for the bands investigated here.

According to formula (5), one finds that the maximum adsorption, which occurs at $\nu=\nu_j$ is given by

$$\epsilon(\max)=\frac{2e^2N}{cm\nu}\frac{f_j}{\nu_j^2}\frac{1}{\gamma_j}$$

or

$$\gamma_j\epsilon(\max)=(2/\pi)\int\epsilon d\nu. \tag{7}$$

Formula (5) has been used here to calculate $\bar{f}$ graphically from the published absorption curves. (7) is used to calculate γ.

If γ were independent of ν throughout the band (an assumption that can always be made for spectral lines), the half width of the band that is the distance between the places where $\epsilon=\epsilon(\max)/2$, would be given by

$$\Delta\nu=(c/\lambda)\Delta\lambda=2\gamma. \tag{8}$$

A comparison of γ calculated by (8) and (7) shows usually differences of not more than 10 percent.

In testing the influence of solvent and chemical substitutions on f, one has to consider that the classical theory predicts an influence of the neighboring molecules due to the Lorentz-Lorenz force, which is the force coming from the polarization of the surrounding molecules. Accordingly, the force acting on one molecule is

$$E+(4r/3)P=E+(4r/3)(n^2-1)E,$$

where P is the polarization per cc, E the field. This results in a replacement in (3) of n^2-1 by $3(n^2-1)/(n+2)$. Assuming a dilute solution, a solvent which has no absorption band at the place where the band of the dissolved compound which is studied is situated, calling furthermore n_0 the refractive index of the solvent at ν, one finds

$$\frac{n^2-1}{n^2+2}=1-\frac{3}{n^2+2}$$
$$=\frac{e^2}{3\pi m}N\left\{\mu_0\Sigma^0+\mu\Sigma\frac{\bar{\bar{f}}_j}{(\nu_j^2-\nu^2)+i\gamma_j\nu}\right\}, \tag{9}$$

where μ_0 is the number of mols of the solvent in 1 liter of the solution and the first sum extends over the absorption bands of the solvent.

If one puts $n=n_0+n'(1-ik)$ a short calculation leads to

$$\epsilon=\frac{e^2}{mc}N\frac{(n_0^2+2)^2}{18n_0}\frac{\bar{\bar{f}}_j\gamma_j\nu^2}{(\nu_j^2-\nu^2)^2+\gamma_j^2\nu^2}, \tag{10}$$

$$\int\epsilon d\nu=\frac{\pi e^2}{cm\nu_j^2}N\frac{(n_0^2+2)^2}{9n_0}\bar{\bar{f}}_j. \tag{11}$$

$\bar{\bar{f}}_j$ is then the transition probability of the dissolved molecules if they were in the gaseous state. This is calculated from the measured value $\bar{f}_j$, the transition probability in solution

$$\bar{\bar{f}}_j=[9/(n_0^2+2)^2]\bar{f}_j \tag{12}$$

[3] Chr. Fuchtbauer, Phys. Zeits. **21**, 322 (1920).

under the assumption, that the Lorentz-Lorenz force is the only modifying influence. In quantum theory, the increase of $\bar{f}$ over $\bar{\bar{f}}$ is due to an increased transition probability induced by the alternating fields of the neighboring polarized atoms.

To see whether, f, $\bar{f}$ or $\bar{\bar{f}}$ are better constants, both have been calculated for some substances measured in sufficiently different solvents (Tables I–XVII).

Results

Tables I–XVII contain the results. The substances have been arranged according to their chemical constitution, λ is the (vacuum) wavelength of the maximum, $\bar{f}$ is calculated from (6), $\bar{\bar{f}}$ from (12), f from (7). The three f's are listed in the order of their size, namely, $\bar{f}, f, \bar{\bar{f}}$. They are given in 10^{-4} electron numbers, so that for example 3000 would correspond to 3/10th of an electron. The γ are in 10^{13} sec.$^{-1}$.

Table I. *Aliphatic compounds.*

Substance	Solvent	λ	f			γ
Iodoform[4]	hexane	3480	449	320	258	8.8
"	"	3052	412	290	234	11
"	ethyl alcohol	3385	445	320	259	9.6
"	" "	2480	423	302	243	12.6
"	chloroform	3479	468	320	242	8.8
"	"	3052	430	290	220	12.1
Ethyl iodide[4]	hexane	2590	13	9	7.2	14.4
" "	chloroform	2560	19.5	13.1	10	16.5
" "	ethyl alcohol	2557	17.1	12.1	10.2	15
" "	water	2510	6.55	4.92	4.10	17
Cyclohexene[4]	heptane	3455	5.85	4.11	3.27	16.2
Tetraethyl ammonium nitrate	chloroform	3125	2070	1410	1080	15
	water	3000	2100	1560	1300	14.2

Table II. *Acids.*[5]

Substance	Solvent	λ	f			γ
Formic	water	2065	28.8	21.6	18.3	26.1
Palmitic	ethyl alcohol	2105	29.5	20.5	16.1	27.2
Butyric	water	2060	31.5	23.7	20.0	27.2
Oxalic	water	2500	19.1	14.3	12.1	19
Succinic	water	2068	45.8	34.0	28.7	22

Table III. *Ketones.*

Substance	Solvent	λ	f			γ
Acetone[4]	hexane	2784	6.05	4.26	3.39	16.9
"	ethyl alcohol	2720	5.75	4.07	3.28	18.6
"	water	2645	6.1	4.6	3.82	18.8
"	water[6]	2648	6.69	4.97	4.19	18.4
"	10% $CaCl_2$ sol.	2609	6.14	4.48	3.68	17.4
Acetylacetone[6]	hexane	2688	4120	2900	2300	16
"	ethyl alcohol	2725	3050	2180	1750	13.6
"	water	2770	1580	1180	975	20.1
Methylacetylacetone[6]	ethyl alcohol or hexane	2864	834	590	474	16.2
"	water	2856	486	360	305	12.7
Menthon[7]	heptane	2893	5.88	4.11	3.25	18
"	methane	2894	6.96	5.17	4.32	14.6
"	ethyl alcohol	2953	7.15	5.11	4.10	14.7
Cyclopentanone[7]	heptane	2953	6.35	4.43	3.35	18.4
"	methanol	2897	6.33	4.68	3.90	18.4
"	"	2910	6.32	4.52	3.64	15.6

[4] G. Scheibe, Ber. d. chem. Ges. **58'**, 586 (1925).
[5] H. Ley and B. Arends, Zeits. f. physik. Chemie **B17**, 177 (1932).
[6] P. Grossmann, Zeits. f. physik. Chemie **A109**, 305 (1924).
[7] H. L. Donle and G. Volkert, Zeits. f. physik. Chemie **B8**, 60 (1930).
[7a] J. Eisenbrand and H. v. Halban, Zeits. f. physik. Chemie **A146**, 234 (1930).

TABLE IV. *Unsaturated compounds and esters.*

Substance	Solvent	λ	f			γ
Acetylacetic ester[6]	hexane	2439	2520	1750	1370	15.6
" "	ethyl alcohol	2457	655	464	373	17
" "	water	2550	42.7	31.9	26.7	18.5
" "	ether	2439	4450	1170	147	15.6
Diethyl acetylacetic ester[6]	ethyl alcohol	2280	206	145	115	21.5
Crotonic ethyl ester[6]	hexane	2470	26.3	18.4	14.6	12.3
" " "	"	1980	5850	3960	3010	15.2
β-ethoxycrotonic ethyl ester[6]	hexane	2289	6150	4260	3340	16
" " "	water	2393	6790	5100	4300	19.7
Acrylic acid[8]	hexane	2419	3160	2210	1750	12.7
Acrolein[8]	hexane	3350	5.04	3.6	2.89	20
"	ether	3350	5.76	4.2	3.46	18
"	ethyl alcohol	3278	5.15	3.7	3.0	21
"	water	3210	8.36	6.2	5.17	20
Crotonaldehyde[8]	hexane	3290	6.25	4.46	3.59	16.4
"	ethyl alcohol	3205	8.35	6.01	4.85	19
Mesetyloxide[4]	hexane	3267	13.4	9.6	7.7	17.2
"	"	2298	3620	2520	1970	13.6
"	methanol	3124	22	15	12.6	18.8
"	"	2380	3480	2520	2060	17
Phoron[4]	hexane	3764	25	18	14.5	15.3
"	"	2590	8430	5900	4670	17
"	ethyl alcohol	3547	40	29	23.7	17.6
"	" "	2635	8190	5800	4860	17
"	water	2727	8570	6350	5240	18.8
"	acetic acid	2666	7380	5500	4620	16.6
"	conc. sulfuric acid	3394	5740	3900	3000	11.5
"	" " "	2750	2300	1400	952	16.8

TABLE V. *Diazo compounds[9] in ethyl alcohol.*

Substance	λ	f			γ
Diazoacetone	3600	4.76	3.45	2.82	11.6
"	2750	1160	828	665	13.8
Diazoacetylacetone	3281	11.1	8	6.5	22
Diazoacetic-methyl ester	3640	5.25	3.8	3.12	
" "	2484	3040	2160	1750	13
Diazoacetic-n-butyl ester	3628	5.20	3.76	3.08	18.3
" "	2510	3760	2670	2140	9.7
Diazomalonic-diethyl ester	3450	7.51	5.43	4.45	13.5
" "	2542	2640	1910	1510	13
" "	3411	7.94	5.7	4.61	20.6
Diazoacetyl-acetic-methyl ester	3700	3.28	2.38	1.95	11.9
" "	2600	1620	1080	716	10
Diazoacetyl-acetic-ethyl ester	3625	6.76	4.9	4.06	13.2
" "	2585	4080	2890	2320	12.1
Diazosuccinic-diethyl ester	3970	4.60	3.4	2.79	13
" "	2530	2100	1490	1240	20.5

[8] A. Luthy, Zeits. f. physik. Chemie **A107**, 285 (1923).

[9] H. Lindermann, A. Walter and R. Gregor, Ber. d. chem. Ges. **63'**, 702 (1930).

TABLE VI. *Aromatic compounds—hydrocarbons.*

Substance	Solvent	λ	f			γ
Benzene	pentane[11]	2685	0.051	0.035	0.027	2.4
"	"	2606	0.68	0.46	0.35	1.7
"	"	2548	0.86	0.57	0.43	1.7
"	"	2486	0.78	0.52	0.40	2.2
"	"	2434	0.3	0.2	0.15	1.5
"	"	2338	0.20	0.13	0.10	2.4
"	"	2289	1.5	0.9	0.8	2.6
"	"	2067	440	278	196	3.4
"	"	2033	730	450	308	5.0
"	"	1878	1100	660	423	6.0
"	heptane[10]	2692	2.98	2.07	1.60	1.0
"	"	2600	4.43	3.06	2.37	1.1
"	"	2546	6.62	4.53	3.50	1.2
"	"	2490	4.72	3.23	2.50	1.2
"	"	2418	3.24	2.27	1.69	1.3
"	"	2384	2.65	1.80	1.39	1.7
"	methanol[10]	2594	3.25	2.37	1.95	1.2
"	"	2543	6.57	4.80	3.94	1.6
"	"	2479	4.42	3.23	2.65	1.2
"	"	2418	2.98	2.16	1.77	1.5
Hexamethylbenzene[12]	hexane	2680	47.9	33.7	26.8	10.5
Toluene[10]	heptane	2765	9.17	6.47	4.99	1.9
"	"	2693	14.8	10.2	7.9	2.3
"	"	2605	8.7	6.04	4.73	3.3
Trimethylbenzene[13]	10n. NaOH	2818	5120	3970	3120	10.5
Ortho-xylene[10]	heptane	2710	12.4	8.60	6.75	2.7
"	"	2640	43.8	30	23.2	7.7
Meta-xylene	"	2721	18.6	12.9	10.1	3.4
"	"	2678	37.4	25.9	20.4	6.2
Para-xylene	"	2750	24.9	17.2	13.5	2.6
"	"	2675	54.7	38	29.7	6.2

TABLE VII. *Chlorides.*[10]

Substance	Solvent	λ	f			γ
Monochlorbenzene	heptane	2720	10.5	7.3	5.7	2.1
"	"	2645	15.7	10.8	8.4	3.2
"	"	2580	21.4	14.7	11.4	5.2
"	methanol	2720	8.8	6.5	5.4	2.4
"	"	2640	14.1	10.3	8.4	3.5
"	"	2558	17.7	12.9	10.6	5.6
Toluolchloride ortho	in heptane	2740	15.5	10.8	8.5	2.5
" "	"	2665	26.6	18.5	14.5	3.7
" "	"	2580	23.0	17.2	13.4	5.3
" meta	"	2743	15.5	10.8	8.5	2.5
" "	"	2700	23.6	16.5	12.9	4.1
" "	"	2653	19.9	13.8	10.8	4.3
" para	"	2761	27.4	19.0	14.9	3.0
" "	"	2702	28.6	19.8	15.6	3.0
" "	"	2631	27.6	19.0	14.8	3.0
" "	"	2580	22.5	15.5	12.0	4.8
Dichlorbenzene ortho	"	2784	15.0	10.4	8.2	1.9
" "	"	2710	28.0	19.4	15.2	3.5
" "	"	2632	28.2	19.4	15.1	5.5
" meta	"	2784	14.8	10.3	8.0	1.5
" "	"	2710	28.0	19.4	15.2	3.5
" "	"	2632	25.0	17.2	13.4	4.7
" para	"	2825	18.6	12.9	10.1	2.0
" "	"	2740	34.2	23.4	18.6	3.3
" "	"	2650	43.8	30.2	23.4	7.2

[10] K. L. Wolf and W. Herold, Zeits. f. physik. Chemie **B13**, 201 (1931).
[11] V. Henri, J. de physique **3**, 181 (1922).
[12] G. Scheibe, Ber. d. chem. Ges. **59**², 2624 (1926).
[13] J. Eisenbrand and H. v. Halban, Zeits. f. physik. Chemie **A146**, 30, 101, 111 (1930).

TABLE VIII. *Nitrocompounds.*

Substance	Solvent	λ		*f*		γ
Nitrobenzene	hexane[12]	3388	26.6	19.0	15.3	10.2
"	"	2515	3480	2670	1930	19.1
"	heptane[10]	2500	4320	2960	2290	19.5
"	ether[12]	3360	37.0	27.0	22.2	11.7
"	"	2565	5250	2580	1260	20
"	methanol[12]	3409[9]	44.3	33.0	27.8	13.7
"	"	2600[12]	3800	2770	2280	21
"	"	2605[10]	3400	2490	2050	19
Chloronitrobenzene ortho	heptane[10]	3365	344	242	193	12.1
" "	"	2430	1780	1210	933	15.5
" meta	"	2970	282	197	156	10.8
" "	"	2500	2520	1730	1340	14.2
" para	"	2660	4500	3100	2400	19
" ortho	methanol[10]	2500	1290	940	775	14.6
" meta	"	2565	3070	2240	1840	19
" para	"	2700	4720	3450	2860	7

TABLE IX. *Phenols.*

Substance	Solvent	λ		*f*		γ
Phenol[10]	heptane	2744	147	102	79.7	2.9
"	"	2710	155	108	84.2	2.5
"	"	2650	155	108	84.2	4.0
"	methanol	2726	529	388	321	1.3
Kresol[10] ortho	methanol	2786	116	86.3	72	2.7
" "	"	2710	289	214	179	6.9
" meta	"	2806	67.5	50.1	41.7	1.7
" "	"	2720	225	164	135	5.6
" para	"	2855	99	77.3	61.4	2.0
" "	"	2793	92.2	68.3	57	2.3
" "	"	2755	204	151	128	5.0
Chlorophenol[10] ortho	heptane	2815	167	116	91	2.9
" "	"	2740	199	138	109	3.4
" "	"	2630	151	108	84	4.3
" para	"	2890	124	86	67.5	2.4
" "	"	2825	137	95	74.6	2.5
" "	"	2750	173	120	94.4	4.3

TABLE X.

Substance	Solvent	λ		*f*		γ
Benzonitril[12]	hexane	2769	37	26	20.7	2.1
"	"	2675	78.2	55	38.8	5.7
"	methanol	2770	52.1	38.6	32.2	3.4
"	"	2700	105.1	77.6	47.1	7.3

TABLE XI. *Ethers.*

Substance	Solvent	λ		*f*		γ
Anisol	hexane[12]	2780	92	64.7	51.5	2
"	"	2710	306	215	171	6.9
"	heptane[10]	2784	64.7	50.5	32.8	2.2
"	"	2722	141	97.8	75.7	2.3
"	"	2650	120	82.7	64	4.2
"	methanol[10]	2784	101	75	62.8	2.8
"	"	2722	148	97.8	78.4	3.0
"	"	2667	146	108	78.4	4.5
"	methanol[12]	2713	226	183	138	7.3
"	water[12]	2710	245	183	154	10
Phenetol[10]	heptane[10]	2784	101	70	54.8	1.9
"	"	2722	17.4	12	9.4	3
"	"	2675	155	108	84.5	4.6
"	methanol[10]	2775	87.5	64.7	54	2.2
"	"	2725	26.4	19.4	16	5.4

Discussion of Methods

Three methods have been used to measure the absorption. *A*. Halban compares the intensity of the light passing through the pure solvent with that passing through the solution with the help of a photoelectric cell. This method can be used in the visible and ultraviolet, is very accurate and needs no assumptions. *B* and *C* are photographic methods in which the spectrum of the light passing through the pure solvent is compared with a series of spectra of the light passing through the solution. This series, printed on the same plate, is either made with different length of exposure t (method *B*, Henri) or with different openings t/t_0 of a rotating sector (method *C*, Scheibe). One determines the exposure time of the spectrum of the solution, that for a certain wave-length gives the same blackening of the plate as the same wave-length passing through the pure solvent, and calculates the absorption from

$$x = q \ln t/t_0,$$

where q is the Schwarzschild constant. This is determined by either printing marks with the source at several distances (method *a*) or by comparison with a photoelectric cell (method *b*).

In the following discussion, the numbers refer to the authors of the bibliography, the letters to the method:

4, 12) method *C*, q determined by *b*. Finds $q=1$, accuracy 1–2 percent.
5) method *B*, use same plates as (4) and assume $q=1$, without mentioning a separate determination.
6) method *B*, says nothing about q.
7) method *C*, follows exactly procedure in 10.
7a, 13) method *A*, accuracy ½ percent.
8) method *B*, says that for his plates $q=0$, 9 (as for Henri, 11).
9) method *C*, do not say anything about q.
10) method *C*, do not say anything about q.
11) method *B*, determines $q=0$, 9 by method a.
14) method *B*, do not say anything about q, but same method as 5. ($q=1$?).
15) method *C*, use $q=1$ without further justification.
16) method *C*; they use $q=1$; comparing their results for potassiumchromate in KOH with Halban (*A*) they find good agreement.
17) method *C*, uses $q=1$. Comparison of the result for pure azobenzene with Halban (*A*), shows good agreement.
18, 19) method *C*, q put equal 1. There is no difficulty as long as it is only a question of stating that the maximum absorption remains unchanged.

Table XII. *Ketones.*

Substance	Solvent	λ	f			γ
Benzophenone[12]	hexane[12]	3450	32.6	23.3	18.7	13
"	"	2484	6150	4300	3410	18.3
"	ethyl alcohol[12]	3270	51.6	37.2	30.5	8.2
"	" "	2550	7350	5280	4240	17.8
"	propyl alcohol[10]	2547	6800	4680	3800	19.4
"	conc. sulfuric acid[12]	3430	45.6	31.0	23.9	11
"	" " "	2960	18800	12000	8550	8.2
Acetophenone[12]	hexane	3204	10.9	7.8	6.3	10.9
"	"	2761	186	131	104	11.2
"	"	2350	3740	2600	2040	14.8
"	ethyl alcohol	3220	9.8	7.04	5.7	8.4
"	" "	2760	195	139	112	13.9
"	" "	2389	3690	2620	2010	14.3
"	water[12]	2770	316	236	195	13.5
"	"	2450	3860	2900	2440	16
"	conc. sulfuric acid[12]	2530	442	267	175	11

Table XIII. *Amines.*

Substance	Solvent	λ	f			γ
Aniline	hexane[12]	2660	422	299	210	10.6
"	heptane[10]	2864	423	296	234	11.0
"	ether[12]	2664	664	366	215	11
"	methanol[10]	2858[7]	378	280	232	13.2
"	"	2806[9]	375	276	231	10.2
"	water[12]	2643	324	240	200	11
Toluidine[10] ortho	in heptane	2850	435	302	237	9.6
" meta	"	2875	385	267	210	9.6
" para	"	2915	379	259	205	9.4
Chloraniline[10] ortho	in heptane	2538	570	416	342	10.6
" meta	"	2538	430	314	258	10.8
" para	"	2585	430	314	258	10.9
" "	"	2155	374	269	218	13.5

TABLE XIV. *Azoxy compounds in alcohol.*

Substance	λ	f			γ
Azoxybenzene[14]	2375	6100	4300	3420	20
Isazoxybenzene[14]	3400	2070	1490	1210	15.5
"	2488	4820	3390	2100	19.4
Azoxytoluene[14] *mm'*	3350	6130	4410	3560	21
Azoxytoluene[14] iso-*mm'*	3310	2300	1660	1340	19
"	2395	5050	3540	2830	22
Azoxytoluene[14] *p-p*	3350	8100	5830	4720	24.0
" iso *p-p'*	3350	3080	2200	1780	21.6
" "	2476	7730	5480	4330	28
Azoxytoluene[15] *o-o*	3150	3820	2670	2120	23.5
" *o-o*-iso-	3220	1320	950	770	14.9
" "	2430	4650	3280	2610	23
Dichloroazoxybenzene[15] *o-o'*-iso-	3120	3580	2500	1990	23
" "	2400	4170	2930	2340	19.4
	3140	1270	890	705	17
	2390	7950	5600	4450	29.6
" *o-o'*	3150	4970	3470	2760	35
Azoxyanisol[14] *o-o'*-iso-	3356	2280	1640	1350	23.4
" "	2410	6740	4740	3370	28.4
Bromazoxybenzene[17] *α*	3352	9040	6500	5260	23
" *β*	3329	10100	7300	5880	24.2
Nitrobromazoxybenzene[17] *α*	3389	11100	8000	6470	23
" *β*	3389	13300	9600	7750	28.9
Nitrobromazoxybenzene[17] *α*	3532	9920	7200	5900	21.6
" *α*	2613	9450	6700	5370	25.4
" *β*	3369	11500	8340	6700	23.8
Azoxybenzene[15]	2375	6100	4300	3420	20
Iso-azoxybenzene[15]	3400	2070	1490	1210	15.5
"	2488	4820	3390	2100	19.4
Azoxytoluene[15] *mm'*	3350	6130	4410	3560	21
Azoxytoluene[15] iso-*mm'*	3310	2300	1660	1340	19.2
"	2395	5050	3540	2830	22
Azoxytoluene[15] *p-p'*	3350	8100	5830	4720	24.1
" iso-*p-p'*	3350	3080	2200	1780	21.6
" "	2476	7730	5440	4330	28
Azoxybenzene-methylether[17] *α*	3507	10500	7200	6220	21.3
" *α*	2490	6980	4950	3980	27.5
" *β*	3332	12800	9200	6460	28
Azoxybenzene-ethylether[17] *α*	3350	9920	7200	5900	20.8
" *α*	2520	4230	3000	2460	17.4
" *β*	3384	13600	9800	7930	28
Oxyazoxybenzene[17] *α*	3545	9520	6900	5650	21.5
" *β*	3332	11200	8060	6520	23
2-methyl-5-oxyazoxybenzene[17] *α*	3957	2880	2100	1730	13.8
" *α*	3260	4450	3200	2590	20.4
" *α*	2803	3500	2500	2020	19.5
" *β*	3229	9100	6550	5300	28

[14] H. Hunecke, Ber. d. chem. Ges. **60**², 1451 (1927).
[15] E. Muller and E. Hory, Zeits. f. physik. Chemie **A162**, 281 (1932).
[16] S. Goldschmidt and F. Graef, Ber. d. chem. Ges. **61**², 1858 (1928).
[17] L. Szego, Ber. d. chem. Ges. **61**², 2087 (1928).

TABLE XV. *Quinones.*[16]

Substance	Solvent	λ	f			γ
Ortho quinone[16]	hexane	3630	955	882	545	16.1
" "	ether	5790	4.63	3.45	2.90	9.3
" "	"	3660	730	531	438	15.2
" "	chloroform	5730	4.95	3.45	2.78	7.8
" "	"	3750	629	430	332	17.0
Homo-ortho quinone[16]	hexane	3655	676	483	277	16.3
" "	ether	5750	4.96	3.70	3.10	11
" "	"	3760	593	430	355	15.3
" "	chloroform	5650	6.42	4.49	3.63	10.2
" "	"	3820	591	405	312	13.4
Paraquinone	hexane	4685	3.96	2.85	2.32	10.6
"	"	2840[12]	1030	730	580	16
"	"	2420[12]	6190	4300	3370	15.5
"	water	4200	6.70	4.85	3.98	14
"	"	2960[12]	993	733	614	15.9
"	"	2490[12]	516	389	327	13.8
β Naphthoquinone[16]	ether	5350	4.62	3.45	2.90	8
"	"	3985	500	367	302	11.2
"	"	3325	415	302	249	9.2
"	"	2495	10700	4400	1112	11.5
"	chloroform	5200	6.70	4.70	3.66	4.8
"	"	4050	550	381	295	11
"	"	3325	455	310	238	8.9
"	"	2300	5230	3450	2550	8.6
"	ethyl alcohol	4000	504	387	302	11.1
"	" "	3370	420	302	244	9
"	" "	2505	6580	4660	3740	13

TABLE XVI. *Miscellaneous compounds.*

Substance	Solvent	λ	f			γ
Pyridin[13]	water	2531	720	540	457	11.4
Betain[13]	water	2631	172	128	108	9
Picolinic acid[13]	water	2617	1540	1150	965	14.2
Sodium picolinate[13]	water	2630	538	401	337	9.4
Nicolinic acid[13]	water	2596	850	834	531	11.6

TABLE XVII. *Pure ketones.*[18]

Substance	λ	f			γ
Acetone	2747	6.87	4.84	3.84	18
Methylethylketone	2770	8.06	5.6	4.37	20
Methylpropylketone*	2790	7.9	5.5	4.4	18.3
Methylisopropylketone	2820	8.8	6.2	4.92	19.5
Methylisobutylketone	2810	8.9	6.2	4.9	18.3
Pinacoline	2810	8.9	5.5	4.9	18.4
Diethylketone	2780	7.8	5.5	4.3	18.4
Ethylpropylketone	2800	8.3	5.6	4.3	18.5
Ethylisobutylketone	2820	9.24	6.2	4.7	19
Dipropylketone	2820	9.24	6.2	4.7	19
Hexamethylketone	2950	8.8	5.9	4.4	18.8

* Same values for methylbutylketone, methylhexylketone, methylnonylketone. $n = 3, 5, 8$.

[18] F. O. Rice, Proc. Roy. Soc. **A91**, 76 (1915).

The use of the photographic methods might introduce systematic errors which, however, probably are not large enough to obviate the general results.

Discussion of Results

Most of the bands contained in the tables are weak bands, relatively few have f's larger than 0.1. Only benzophenone in concentrated sulphuric acid and some of the nitroazoxybenzene compounds have f's larger than 1. The large value of f for a band in the near ultraviolet (region of 3500A) in nitrobenzene and some of the azoxybenzenes of Table XV account for their high refractive index and dispersion.

In an attempt to find regularities the first impression is that no rules that are valid without exception can be deduced from the tables. Variation of the solvent shows that it is impossible to account for the influence of the solvent through the Lorentz-Lorenz force. The following is a compilation of the results.

For the solutions of iodoform (Table I), mesetyloxide (Table IV), benzene* (Table VI), acetophenone in hexane and alcohol (Table XII), the variations of the refractive index of the solvent are too small to permit a distinction between the equally good agreements of $\bar{f}$, f, $\bar{\bar{f}}$.

For ethyliodide (Table I), acetyl- and methylacetyl acetone (Table III), acetophenone in water and the esters (Table III), the ethers (Table XI), benzophenone (Table XII), the quinones (Table XVI), the variation in the three quantities $\bar{f}$, f, $\bar{\bar{f}}$, is about equally large.

For tetraethylammoniumnitrate in chloroform and water (Table I), aceton (Table III), ethoxycrotonic ethylester and phorone (Table IV), $\bar{f}$, f are decidedly better constants than the value following from the Lorentz-Lorenz force, $\bar{\bar{f}}$. For nitrobenzene (Table VIII), f is best.

In the amines of (Table XIII) however $\bar{\bar{f}}$ is by far the most constant.

For crotonaldehydes (Table IV) and benzonitril (Table X) the values of f/γ which give the height of the maximum of the absorption curve, seem better constant than any one of the f's alone. This fact had already been remarked by F. O. Rice,[18, 19] who measured ketones in the pure form (Table XVI) and in solution, and found the height of the absorption curve the same.

In discussing the influence of substitutions it makes no difference which one of the f's we use because they differ by a factor referring to the solvent.

It is found in general that a substitution of Cl or CH_3 for H increases the f for the bands which have nearly the same wave-length in spite of the fact that for this reason these bands belong probably to a part of the molecule not directly affected by the substitution. Examples are found in the comparison of benzene and toluene (Table VI) of monochlorbenzene with toluene chloride and dichlorbenzene (Table VII). Very often we have for f

$$\text{meta} \leqq \text{ortho} < \text{para}.$$

This can be seen in xylol (Table VI), the chlorides (Table VII), the nitrocompounds (Table VIII) which have, however, meta > ortho.

In the phenols of (Table IX) however, we have

$$\text{ortho} > \text{para} > \text{meta}.$$

Here again f/γ (the maximum of absorption) seems better constant than anything else. We have also

$$\text{ortho} > \text{meta} = \text{para}$$

for toluidin and chloraniline (Table XIII).

In the fatty acids (Table II) f and γ are very accurately constant, while the values for oxalic and succinic acid are considerably different.

* There is strong disagreement between benzene in pentane and heptane. These two solutions have been measured by different authors.

[19] F. O. Rice, J. Am. Chem. Soc. **42**, 2665 (1920).

Photochemical Studies. XVIII
The Fluorescence of Acetone Vapor

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A thorough understanding of the photochemical decomposition of acetone vapor must be accompanied by a study of the fluorescence of this substance. Previous work had indicated that the fluorescence is relatively weak, is affected by oxygen and (at least over part of the spectral range involved) possessed a fine structure. In the present work it is shown that the intensity of the fluorescence follows the customary behavior observed in such phenomena in that it is quenched by the acetone vapor itself. A discussion is given as to the relationship of the fluorescence to the possible modes of photochemical decomposition.

THE fluorescence of acetone vapor has been observed by Damon and Daniels.[1] These authors state that the energy emitted in this way is a small fraction (perhaps much less than three percent) of the absorbed energy. Crone and Norrish[2] find that the fluorescence of acetone lies in the visible part of the spectrum and is diffuse. They interpret this as "predissociation in emission."

The possible interpretations of the photochemical decomposition of acetone vapor have been discussed by several authors.[3] To summarize very briefly two mechanisms may be postulated: (1) after absorption of radiation carbon monoxide and ethane (the principal products) may be produced in one step by a unimolecular process; (2) free radicals may be formed, the course of the reaction being determined by the nature of the reaction chain.

Damon and Daniels[1] find that the quantum yield is low, increases at low intensities, decreases at low pressures and remains independent of wave-length between 3130 and 2650A.[4] The increase at low intensities favors the hypothesis of free radicals and the decrease at low pressures indicates that the decomposition may not be unimolecular but of the type of predissociation by collisions.[5]

Norrish and Appleyard[3] state that there is a sharp threshold of fluorescence near the beginning of the absorption spectrum and that in the region of diffuseness beyond 3000A there is no trace of fluorescence even at low pressure. This fact would be difficult to reconcile with a quantum yield strictly independent of wave-length.

It is evident that a complete understanding of the photochemical decomposition of acetone vapor necessitates a thorough study of the fluorescence. The spectroscopic aspects of this phenomenon have been studied by others, so that we have confined ourselves to an investigation of the intensity of the fluorescence with varying experimental conditions.

A. Experimental Procedure

As pointed out by Damon and Daniels[3] the fluorescence of acetone vapor is weak and is markedly affected by the presence of oxygen, the color changing from green to blue when this substance is present.

As a source of exciting radiation a capillary mercury arc lamp similar to that described by Forbes and Harrison[6] was employed. A crystal quartz prism and crystal quartz lenses, together with a suitable slit system were used to furnish monochromatic radiation of wave-length 3130A. Since the quantitative formulation of the law

[1] G. H. Damon and F. Daniels, J. Am. Chem. Soc. **55**, 2363 (1933).

[2] H. G. Crone and R. G. W. Norrish, Nature **132**, 241 (1933). In a private communication Dr. Norrish has stated that the discrete ultraviolet fluorescence previously reported has not been confirmed.

[3] See G. H. Damon and F. Daniels, reference 1; F. W. Kirkbride and R. G. W. Norrish, Trans. Faraday Soc. **27**, 407 (1931); R. G. W. Norrish, ibid. **30**, 103 (1934); R. G. W. Norrish and M. E. S. Appleyard, J. Chem. Soc. **1934**, 874; W. A. Noyes, Jr., Rev. Mod. Phys. **5**, 280 (1933).

[4] See, however, R. G. W. Norrish, H. G. Crone and O. D. Saltmarsh, J. Am. Chem. Soc. **56**, 1644 (1934) who state that the yield is not strictly independent of wave-length.

[5] See W. A. Noyes, Jr., reference 3.

[6] G. S. Forbes and G. R. Harrison, J. Am. Chem. Soc. **47**, 2449 (1925).

governing the fluorescence necessitates highly monochromatic radiation, in some experiments color filters were employed in conjunction with the monochromator. For this purpose potassium chromate was usually employed, although Red Purple Corex glass was used in one experiment. By rough experimental test radiation of wavelengths other than those at 3130A amounted to less than one percent of the total. Fluorescent screens were used for focussing the monochromator.

The intensity of the incident radiation was measured by a photoelectric cell (caesium-caesium oxide cell with quartz envelope) placed either directly back of the absorption cell or arranged so that it could be moved into a reproducible position in front of the absorption cell. The beam of incident radiation was diaphragmed in such a way that it was entirely intercepted by the photoelectric cell.

A T-shaped fluorescence cell was used, the incident radiation passing through the horizontal portion. Plane fused quartz windows were attached with picein wax. Below the lower limb at a distance of about 8.5 cm was placed a metal plate perforated by a hole 3 mm in diameter behind which could be placed a photographic plate protected by a shutter. A piece of plate glass was interposed to absorb scattered 3130A radiation. The fluorescence falling in the spectral range from about 4000A to the long wave limit of an Eastman 33 plate was studied.

Blanks were always made with no acetone in the cell to make sure that scattered radiation was unimportant. Corrections were always made for scattered radiation, but they amounted to less than experimental error.

The photographic plate was exposed to the fluorescent radiation for a specified length of time, five or six spots being made under varying conditions of pressure, incident intensity, etc. Subsequently spots were placed on the plate by radiation of known relative intensity. For this purpose a small hole illuminated by a 10 watt lamp protected by a Wratten green filter was used as a standard source and the inverse square law for intensities assumed. The spots due to the standard radiation were always placed near the spots made by the fluorescent radiation, although the uniformity of the emulsion was such that this precaution was hardly necessary. The length of exposure of the fluorescence was always very nearly the same as for the standard.

The blackening of the spots was then measured by means of a photoelectric cell, by using a beam small compared to the diameter of the spot. By having several standard spots of varying degrees of darkening the interpolation did not extend over a wide range of intensity.

The acetone had been specially purified in the laboratory of Professor Kraus for solubility work. It was further purified by fractional distillation at low pressures.

The intensity of the fluorescent radiation has been studied as a function of the incident intensity, and the acetone pressure. Since oxygen affects the fluorescence, the acetone in the present experiments was thoroughly outgassed by evacuation with a mercury diffusion pump while condensed with liquid air. In appearance the fluorescence was always greenish.

B. Results

In order to show how the results were calculated we will illustrate by means of one run given in detail.

The absorption coefficient for 3130A radiation is 6.63 (concentration in moles per liter, distance in centimeters).[7] The length of path from which radiation could be incident on the photographic plate is 2 cm (beginning 2 cm from the incident window) and the over-all length of the absorption cell is 6.5 cm.

The data of Table I were obtained in one run.

A plot is now constructed of log B/A *vs.* I_s. For the spots log B/A should be a numerical measure

Table I.

Pressure (cm)		5.2		8.6	10.8	14.9		18.9
Galv. deflection (transmitted light)		2.05		1.89	1.73	1.57		1.45
Absorbed in element 2 cm in length		0.0842		0.134	0.158	0.211		0.260
Distance of standard (cm)	25	35	40	45	50	55	60	70
Deflection through spot (A)	2.50	4.50	5.75	7.30	8.50	9.40	9.95	10.50
Deflection through plate near spot (average) (B)	10.93	10.95	10.87	11.12	11.10	11.17	11.15	11.20
Intensity I_s (50 cm = 1)	4.00	2.04	1.56	1.23	1.00	0.827	0.695	0.510

[7] Cf. reference 1; C. W. Porter and C. Iddings, J. Am. Chem. Soc. **48**, 40 (1926).

TABLE II.

Pressure (cm)	5.2	8.6	10.8	14.9	18.9
Deflection through spot (A_1)	9.95	9.45	9.20	8.55	7.90
Deflection through plate near spot (average) (B_1)	10.90	10.95	11.07	11.10	10.93

of the darkening. The data of Table II were obtained for the spots produced by the fluorescent radiation.

By comparing log B_1/A_1 with the graph previously constructed the following relative intensities are obtained (the intensity of the standard radiation at 50 cm = 1)

Pressure (cm)		5.2	8.6	10.8	14.9	18.9
Relative intensity	I_f	0.62	0.78	0.85	0.99	1.09

In those experiments in which the incident intensity was varied, various thicknesses of Pyrex glass or of cellophane were placed in front of the entrance slit of the monochromator. Otherwise the method was identical with that described above.

In presenting the results in detail it seems wise at first to give a possible elementary theory of the fluorescence. The mechanism may be represented by the following reactions:

$$Ac+h\nu=Ac', \tag{1}$$

$$Ac'=Ac+h\nu', \tag{2}$$

$$Ac'+Ac=2Ac. \tag{3}$$

If D_1 is the galvanometer deflection due to the radiation incident on the volume element from which the fluorescent radiation is to be studied then the incident intensity is

$$I_1=k_1D_1, \tag{4}$$

where k_1 is a proportionality constant necessary for converting deflection units into the desired units of intensity. The total radiation absorbed in the volume element will be

$$I_a=I_1A(1-\exp(-kcl)), \tag{5}$$

where A is the area of the beam and l is the length of the volume element. k is the absorption coefficient (6.63 as given above). The rate of formation of excited acetone molecules (in the entire volume element, not per unit volume) will be

$$+d(Ac')/dt=k_2I_a=k_2k_1D_1A(1-\exp(-kcl)). \tag{6}$$

The rate of disappearance of excited acetone molecules will be

$$-d(Ac')/dt=k_3(Ac')+k_4(Ac')(Ac), \tag{7}$$

where (Ac') and (Ac) represent the numbers of excited and normal acetone molecules in the volume element (not per unit volume). Since the number of excited molecules is at any instant very small and since in the present experiments photochemical decomposition was never appreciable we may write

$$(Ac)=K_1P, \tag{8}$$

where P is the total pressure of the acetone. By equating (6) and (7) (for the steady state) and substituting by Eq. (8) we obtain

$$(Ac')=k_1k_2D_1A(1-\exp(-kcl))/(k_3+k_4K_1P). \tag{9}$$

But the intensity of the fluorescent radiation will be

$$K_2k_3(Ac')=I_f=K_2k_3k_1k_2D_1A(1-\exp(-kcl))/(k_3+k_4K_1P), \tag{10}$$

where K_2 is a proportionality constant necessary for converting the number of acetone molecules in the volume element which lose their energy by fluorescence per second to the arbitrary units used for measuring the intensity of the fluorescence. Hence

$$D_1(1-\exp(-kcl))/I_f=1/k_1k_2K_2A+k_4K_1P/k_1k_2k_3K_2A. \tag{11}$$

It will be seen from Eq. (11) that if the simple mechanism given above for the fluorescence is adequate a plot of $D_1(1-\exp(-kcl))/I_f$ *vs.* P should give a straight line. Fig. 1 shows two such plots for typical runs.

Since for a given run all of the quantities in Eq. (11) are constant except D_1, I_f, c and P, it follows that the slope divided by the intercept is k_4K_1/k_3. k_3 is a first order constant and should depend only on the time units chosen. Since K_1 is a constant which relates pressure to the number of molecules in the volume element it will remain constant as long as the geometry of the system is unchanged. k_4 is the fraction of the excited acetone molecules deactivated per unit time per molecule of acetone present in the

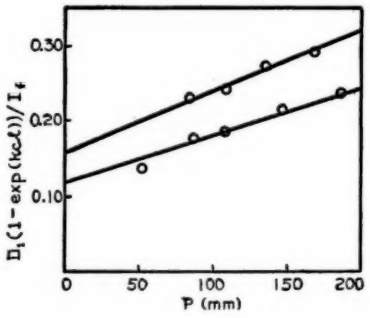

FIG. 1.

volume element. k_4K_1 is the fraction of the excited acetone molecules deactivated per unit time at unit pressure by collision. Both k_4K_1 and k_3 will be independent of the geometry of the system and the slope divided by the intercept should not change from one run to another even though the shape of the beam might vary somewhat.

Table III gives the data obtained during the last five runs obtained after most of the experimental difficulties had been removed.

TABLE III. *Variation of fluorescence with pressure.*

Pressure (cm)	7.1	10.2	13.7	16.6	18.9
$D_1(1-\exp(-kcl))$	0.0314	0.0663	0.0868	0.101	0.110
I_f	1.72	1.82	2.07	2.28	2.45
Slope/intercept	0.053				
Pressure (cm)	5.4	9.7	12.9	15.8	17.9
$D_1(1-\exp(-kcl))$	0.038	0.064	0.082	0.097	0.108
I_f	0.30	0.42	0.49	0.56	0.58
Slope/intercept	0.052				
Pressure (cm)	5.2	8.6	10.8	14.9	18.9
$D_1(1-\exp(-kcl))$	0.084	0.1	0.158	0.210	0.260
I_f	0.62	0.78	0.85	0.99	1.09
Slope/intercept	0.054				
Pressure (cm)	3.3	6.7	10.1	18.2	18.4
$D_1(1-\exp(-kcl))$	0.036	0.072	0.103	0.173	0.191
I_f	0.29	0.55	0.68	0.79	0.91
Slope/intercept	0.050				
Pressure (cm)	8.5	10.9	13.5	16.8	
$D_1(1-\exp(-kcl))$	0.351	0.447	0.606	0.743	
I_f	1.54	1.86	2.24	2.57	
Slope/intercept	0.049				
Average slope/intercept	0.052				

Inspection of Eq. (11) shows that $D_1(1-\exp(-kcl))$ plotted against I_f at constant pressure should give a straight line passing through the origin. Four runs were made at a pressure of 121 mm to test this point. A straight line plot was obtained in every case, although it did not quite pass through the origin in two of the four experiments. The actual ratios of $D_1(1-\exp(-kcl))/I_f$ are given in Table IV.

TABLE IV. *Variation of fluorescence with incident intensity.*

$D_1(1-\exp(-kcl))$ (M)			1.96	1.37	0.90	0.53
$D_1(1-\exp(-kcl))/I_f$ (N)			1.0	1.0	1.0	1.0
M	1.68	1.26	0.95	0.71		
N	1.9	1.8	1.7	1.9		
M	2.53	1.56	1.47	0.65		
N	1.5	1.3	1.3	1.1		
M	3.45	2.00	1.22	0.86	0.59	
N	1.4	1.5	1.3	1.2	1.0	

C. DISCUSSION

To a first approximation Eq. (11) seems to agree with the experimental facts. The theory upon which this equation is based is obviously inadequate. At 25°C acetone molecules will exist in a variety of vibration and rotation energy levels and many levels must be formed by the absorption of radiation contained in the group of lines at 3130A. A detailed statistical theory would be necessary for a rigorous explanation of the experimental facts. Unfortunately not enough information is available to permit such a study to be made, even if it were possible to carry out the necessary mathematical manipulations.

Let us examine a little more fully the conclusions which may be drawn from the simple theory upon which Eq. (11) is based and then point out the modifications which would be necessary for a more complete theory. The number of collisions per excited acetone molecule per second at a pressure of one centimeter is

$$Z_e=4.78\times10^{22}\sigma^2 \qquad (12)$$

at 25°C, where σ is the distance between centers at the time of "collision." If every collision is effective in deactivating an excited molecule, the rate of deactivation will be

$$-d(Ac')/dt=4.78\times10^{22}\sigma^2(Ac')P, \qquad (13)$$

where P is the acetone pressure in centimeters. If J_a is the number of quanta absorbed per second in the volume element and J_f is the number of quanta emitted as fluorescence from the volume element per second we may write

$$J_a/J_f=4.78\times10^{22}\sigma^2P/k_3+1. \qquad (14)$$

Eq. (14) is analogous to Eq. (11). Since the arbitrary units used in measuring the light

intensities cancel out in dividing the slope by the intercept in Table III, we may write

$$0.05 = 4.78 \times 10^{22} \sigma^2 / k_3. \qquad (15)$$

The value of σ is not known, but may be taken as approximately 5×10^{-8} cm. This gives $k_3 = 2.4 \times 10^9$ sec.$^{-1}$ and the mean life of the excited acetone molecule would be 4×10^{-10} sec. It is true that by introducing an efficiency factor for collisions into Eq. (12) or by reducing the value of σ one can cause an increase in the value obtained for the mean life, without, however, changing in any essential respect the considerations in the following paragraphs. 4×10^{-10} sec. may be considered as a minimum figure.

From the figures given in the preceding paragraph one can calculate the fraction of the absorbed energy which should be reemitted in the form of fluorescence at a pressure of 250 mm, where Damon and Daniels[1] observed this fraction to be less than 0.03. Calculation shows that the number of emitted quanta should be about 45 percent of the number of absorbed quanta.

The discrepancy between the observed and calculated values is beyond the limits of experimental error and necessitates a modification of the theory. One might assume, for example, that a series of upper states are formed each with its own specific rates of fluorescence and deactivation. Each of the members on the right side of Eq. (7) would then be replaced by a summation. The problem would be hopelessly complex unless it is assumed that the relative rates of formation of the molecules in the various states remain independent of pressure. A superficial examination will indicate, however, that this method of approach will not resolve the difficulty made apparent in the preceding paragraph.

One other obvious method of approach suggests itself in that Eqs. (1), (2) and (3) take no account at all of the photochemical decomposition. This decomposition may result either by a first order step or by a second order step involving predissociation by collision. The photochemical evidence is not unambiguous on this point. However since Eq. (11) seems to account satisfactorily for the fluorescence data, the introduction of the photochemical decomposition must not alter the form of this equation and yet it must provide a mechanism whereby the amount of fluorescence will be decreased. This can be done by introducing a fourth step

$$Ac' = D, \qquad (16)$$

where D represents dissociation products. Let the specific rate constant for this reaction be k_5. It can now be shown that the slope divided by the intercept will be $k_4 K_1/(k_3+k_5)$. Thus $(k_3+k_5) = 2.4 \times 10^9$. By using a value of the quantum yield one can now calculate an upper limit to the fraction of the absorbed radiation which should appear as fluorescence. If the quantum yield is taken as 0.3, the maximum fraction of the incident quanta which could appear as fluorescence is 0.14. (Since the wave-length of the fluorescence radiation is longer than that of the incident radiation, the fraction of the *energy* reemitted would be between 0.07 and 0.10.) There is the further possibility, as suggested by Norrish and his co-workers,[4] that some internal rearrangement may take place unaccompanied by either fluorescence or decomposition.

In conclusion it should be exphasized that this mechanism will not account for a decrease in quantum yields at low pressures. Indeed by including a short chain reaction or by introducing predissociation by collisions to account for a *small* fraction of the photochemical decomposition the above results would not be seriously modified. The slight decrease in yield at high intensities[1] argues strongly for the existence of reaction chains.[8]

There seems to be some disagreement among various workers as to whether fluorescence is of equal importance for all incident wave-lengths.[9]

The authors wish to express their appreciation for a grant-in-aid obtained from the National Research Council which aided materially in pursuing this and related investigations.

[8] See J. A. Leermakers, J. Am. Chem. Soc. **56**, 1537 (1934) for a discussion of the very analogous case of acetaldehyde in which two types of decomposition seem to take place at room temperature.

[9] Cf. reference 1; R. G. W. Norrish, Nature **133**, 837 (1934).

On the Question of "Afterburning" in Gas Explosions[1]

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The works of David, Brown and El Din, Ellis and Morgan, and Ellis and Wheeler on "afterburning" have been reviewed critically and found to contain no conclusive evidence for "afterburning." Experiments have been performed on explosions of hydrogen-oxygen mixtures with different inert gas in spherical vessels of different sizes which show, on the contrary, the absence of this phenomenon. The explosion method for determining heat capacities of gases may not be criticized on this account.

THE explosion method is the only direct experimental method for determining heat capacities and dissociations of gases at high temperatures. A suitable combustible gas mixture is ignited at the center of a spherical vessel, and the maximum pressure developed is measured. This method was first proposed by Bunsen and since the mastery of the main technical difficulties by Pier[4] in 1908 it has been applied with marked success in a number of investigations. In the last few years objections have been raised to the explosion method by several investigators whose work will be discussed below.

Because it is of considerable importance to clarify the status of this experimental method, we shall endeavor to review critically the three most important papers which concern the subject. These are by David, Brown and El Din,[5] and Ellis and Morgan,[6] and Ellis and Wheeler.[7] From their experiments these investigators conclude that when a combustible gas mixture is ignited at the center of a spherical vessel the combustion is still incomplete in the burned gas when maximum pressure is established. Thus the term "afterburning" has come into being.

It will be shown in this paper that the evidence presented in the above papers is not valid.

DAVID, BROWN AND EL DIN'S INVESTIGATIONS

These investigators exploded identical dry mixtures of hydrogen and air and carbon monoxide and air plus one percent hydrogen in two spherical vessels of different sizes—6 inches and 17.45 inches in diameter. Time-pressure records were obtained in the usual way, using a diaphragm developed by Thorp.[8] At the same time a platinum bolometer was placed at the wall to measure the heat lost to the wall during the progress of the explosion.

In the carbon monoxide explosions heat losses totaling 1.5 to 6 percent were found, with generally higher losses in the small vessel (except for the weakest mixture), whereas in the hydrogen explosions the measured heat losses were negligibly small. In both sets of experiments, after corrections for heat losses were made, the ratios of the maximum pressure to the initial pressure were appreciably higher in the large than in the small vessel.

Since this result may not be accounted for by the relative heat losses according to their measurements, the authors conclude that "combustion is more complete at the moment of maximum pressure in the large vessel than in the smaller one, and if this is so, it is hardly likely that combustion is complete, even in the large vessel.[9]"

These results confirm the pioneer experimental work of Pier, who in his very first set of experiments[4] discovered that the maximum pressures established in an 18-inch vessel were considerably

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[4] Pier, Zeits. f. physik. Chemie **62**, 385 (1908); Zeits. f. Elektrochemie **15**, 536 (1909).
[5] David, Brown and El Din, Phil. Mag. **14**, 764 (1932).
[6] O. C. de C. Ellis and E. Morgan, Trans. Far. Soc. **30**, 287 (1934).
[7] O. C. de C. Ellis and R. V. Wheeler, J. Chem. Soc. 310 (1927).
[8] Thorp, Phil. Mag. **8**, 813 (1929).
[9] They infer the latter part of the statement from their unpublished results in a 12-inch vessel.

greater than in a 6-inch vessel, for identical mixtures. Pier, on the other hand, ascribed these differences to excessive heat losses in the small vessel. Considering certain features of Pier's (and also David *et al.'s*) experimental arrangement, it seems more than likely that the kind of heat losses responsible for the difference in maximum pressures found in 6- and 18-inch vessels escaped detection in the method of David, Brown and El Din. It is to be borne in mind that although the explosion vessels used in Pier's and David and co-workers' experiments were in general spherical, they contained pockets under the diaphragm and possibly the gas valves which were outside the general spherical contour of the interior of the vessel. (Compare Pier[4] and Thorp[8]; David and co-workers employed Thorp's technique.) During the explosion, unburned gas is compressed into these pockets, and when the flame reaches the wall and the cooling process begins, they contain unburned gas at practically maximum pressure. While the percentage of the initial gas mixture thus trapped is negligible in any large vessel, it may no longer be neglected in a small vessel. Suppose, for example, the pocket volume amounts to only 0.4 percent of the total volume of a 6-inch vessel (1765 cc) and consider an explosion in which the pressure increases some eightfold. The amount of unburned gas compressed into the pocket space when the flame reaches the spherical wall amounts to approximately two percent of the total initial charge (allowance being made for heating due to adiabatic compression). If the pocket has a depth of ten percent of the radius, the time required to burn its contents may easily be of the order of ten percent of the total explosion time, during which interval enough cooling has taken place along the spherical wall to render ineffective, as far as pressure rise is concerned, subsequent burning of the pocket gas. Another important source of heat loss may easily arise from eccentricity of the ignition source. This is of special importance in a small vessel, where the percentage of eccentricity is apt to be larger. Thus, since a portion of the flame touches the wall first, the maximum pressure is lowered. Couple these two sources of heat losses with the fact that the rate of cooling due to heat conductivity at the spherical wall is greater in the smaller vessel[10] and it is not difficult to envisage the cause of the experimental pressure differences found by David and co-workers.

To make a fair comparison two spherical vessels should be used, of such size as to render losses due to pockets and eccentricity of the ignition source (if the former are not eliminated entirely) negligible; yet they should differ sufficiently in size to enable one to detect any effect attributed to the cause proposed by David and co-workers.

We have carried out this comparison in two cast-iron spherical vessels in which pocket space was negligibly small (less than 1 cc). The diaphragm was made of monel metal and has been described elsewhere.[11] It was calibrated very carefully dynamically and statically and found to check perfectly our calibration of two years ago. As published previously, dynamic and static calibrations were identical, and no hysteresis whatsoever was observed with a diaphragm of this type. Absolute pressures could be relied on within 0.15 pound, or about 0.20 percent in the range 90 to 100 pounds. Since the diaphragm proper is not clamped to the wall of the vessel, the tension of the diaphragm is not affected by expansion or contraction of the vessel as a whole. Therefore calibrations made at the different initial temperatures encountered in these experiments were identical.

Atmospheric air was dried over calcium chloride and magnesium perchlorate. The "air" used in David *et al.*'s experiments contained only 19.9 percent oxygen and an unknown amount of argon. Therefore, our maximum pressures are not strictly comparable with theirs, but the small differences between their large vessel explosions and ours are in the direction to be expected.

After each explosion the vessel was evacuated to 2 mm and flushed twice with hydrogen to insure that the water-vapor pressure was below 0.001 mm Hg.

The results are tabulated in Table I, the ratio of the maximum to the initial pressure (Pe/Pi) being corrected to 20°C in the same manner as

[10] In the range 30 percent hydrogen in air and higher, we find the rates of cooling are approximately inversely as the square of the radii.

[11] Lewis and von Elbe, J. Am. Chem. Soc. **55**, 504 (1933).

TABLE I. *Ratios $(Pe/Pi)_{20°C}$ of hydrogen-air explosions in 17.72-inch and 11.81-inch spherical vessels.*

17.72-inch vessel			11.81-inch vessel		
Hydrogen in air, percent	Initial temperature before explosion, °C	$\left(\frac{Pe}{Pi}\right)_{20°C}$	Hydrogen in air, percent	Initial temperature before explosion, °C	$\left(\frac{Pe}{Pi}\right)_{20°C}$
			16.53	20.72	5.946
			17.50	21.48	6.195
18.08	23.50	6.310	18.97	22.08	6.492
19.98	21.97	6.694	19.99	22.84	6.704
32.01	22.77	8.114	31.99	21.28	8.126
45.01	22.12	7.434	44.98	21.70	7.426
60.00	22.67	6.175	59.96	21.60	6.176

were David *et al.'s* results. Pi was always 720 mm Hg.

The ratios $(Pe/Pi)_{20°C}$ are plotted in Fig. 1 against percent of hydrogen in air.

The two series of experiments agree very well. This shows that the results of David and co-workers cannot be used as evidence for "afterburning."

If any difference exists at all the explosion pressures should be slightly higher in the smaller vessel, due to the existence of a time lag in the excitation of the vibrational energy states of nitrogen and oxygen molecules,[12, 13] an effect which should be more marked for shorter explosion times. The slight differences between both series may be so interpreted. Later[13] we shall compare quantitatively the observed explosion pressures with those to be expected if the vibrational energy states were fully excited during the explosion process.

Measurements of the explosion times showed that they were proportional to the radius, as is to be expected. For example, for the 32 percent mixture the times in the large and small vessels were 0.01405 second and 0.00952 second, respectively, or a ratio of 1.475; for the 60-percent mixture the times were 0.0306 and 0.0206 second, or a ratio of 1.485. The ratio of the radii was 1.50. This is about one-half the ratio of the radii of the two vessels used by David and co-workers; therefore, considering the magnitude of the effect found by them it should have sufficed to show the effect of "afterburning" if it existed. That a comparison of the 12-inch and 18-inch spheres is sufficient also is indicated by these workers.

[12] Wohl and Magat, Zeits. f. physik. Chemie **B19**, 117 (1932).

[13] To be published.

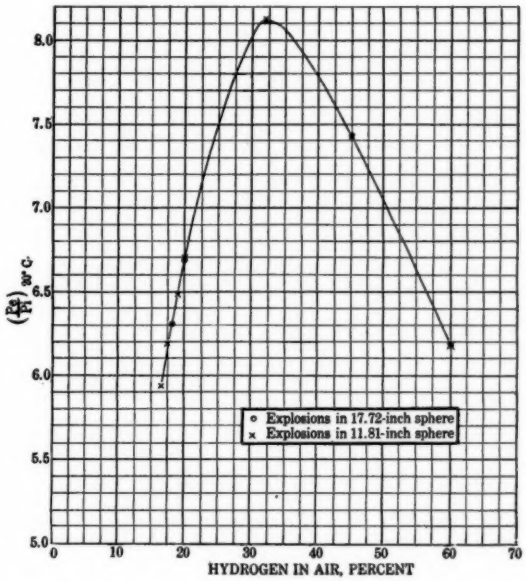

FIG. 1. Ratios of maximum to initial pressure in explosions of different mixtures of hydrogen and air in spherical vessels of different sizes.

ELLIS, MORGAN AND WHEELER'S INVESTIGATIONS

The experiments of Ellis and Morgan on the temperature gradient in the burned gas within a spherical flame in a closed vessel confirmed the results of previous investigators[14] that the temperature is highest in the center and decreases outward. The reason for this may be understood readily from simple qualitative considerations,[14a, 15, 16] which we shall repeat here.

An elementary mass of gas at the center burns by expanding at practically constant pressure Pi. Subsequently it is compressed to nearly its original volume by combustion of the rest of the gas in the vessel. The latter work of compression exceeds the former work of expansion because the compression of the elementary mass takes place at a steadily increasing pressure from Pi to Pe, while expansion takes place at the lowest pressure Pi. An elementary mass of gas near the wall, on the other hand, is first compressed under a pressure which rises from Pi to Pe and then expands (on combustion) to approximately its original volume at maximum pressure Pe. The

[14a] Hopkinson, Proc. Roy. Soc. **A77**, 387 (1906). [b] Ellis and Wheeler, J. Chem. Soc. 2467 (1931).

[15] See Flamm and Mache, Wien. Ber. **126**, 9 (1917), and Mache, *Die Physik der Verbrennungserscheinungen*, 1918.

[16] Lewis and von Elbe, J. Chem. Phys. **2**, 283 (1934).

latter work of expansion obviously is larger than the former work of compression. Thus, the elementary mass of gas near the wall loses some of its energy while the elementary mass of gas in the center gains energy in addition to the chemical energy released within it. The result is the establishment of a temperature gradient which rises from the wall to the center and is accompanied by a density gradient of opposite sign. This is also the case if the flame has progressed only part of its total final distance.

It is of interest to note the effect of the temperature gradient on the rate of pressure decrease after an explosion in a spherical vessel with central ignition, which is readily observed but has not, to our knowledge, been described in the literature. The first rapid drop immediately after the establishment of maximum pressure is due to the cooling of the hot gases near the wall. The subsequent pressure drop takes place at a reduced rate because of the slower transfer of heat to the wall through these cooled layers. When the heat stored in the center of the sphere reaches the outer layers, heat transfer to the wall is momentarily increased and a second rapid drop in pressure occurs. This inflection in the cooling curve may always be observed. It is especially marked in mixtures which possess high heat conductivity, for instance, explosions of hydrogen and oxygen with helium as inert gas, of which the photograph in Fig. 2 is an example. In mixtures with low heat conductivity it is drawn out over a very long portion of the cooling curve.

The slope of the temperature gradient may be calculated quantitatively from Flamm and Mache's equations when the heat capacities and equilibrium constants are known. Such calculations were made by the present authors for explosions in gaseous ozone and hydrogen-oxygen mixtures[16, 17] and also by Flamm and Mache[15] for a mixture of hydrogen and oxygen with excess hydrogen. Although the latter investigators made their calculations with heat capacities which are not considered quite accurate today and neglected the effects of dissociation, their results and ours as well provide an insight into the magnitude of the effects to be expected. The temperature difference at maximum pressure between the gases at the point of ignition (in this case the center of a sphere) and the gases in the layer last burned (near the wall) was found to be about 800°C in their calculation for a mixture of approximately $7H_2+O_2$. For the cases which we calculated, temperature differences ranging from 600 to 900°C were found.[17]

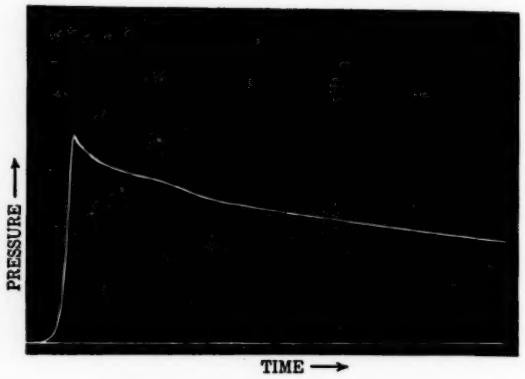

FIG. 2. Effect of temperature gradient on cooling curve.

We note, however, that Ellis and Morgan have also derived an expression for the temperature gradient in a sphere for the case of complete combustion behind the flame front, that is, no "afterburning." They reach the conclusion that under these conditions the temperature should *decrease* from the flame front inward and is a minimum at the center where ignition takes place, which is the opposite conclusion reached from the above reasoning. Having established experimentally that the temperature *increases* toward the center they conclude that "'afterburning' is independently demonstrated in a new way."

Now, on examining their derivation[18] of the temperature gradient one finds that their final equation demands a pressure gradient along with a temperature gradient and a density gradient. Their final equation can be written

$$\left(\frac{P}{P_B}\right)^{(\gamma-1)/\gamma}=\left(\frac{\rho}{\rho_B}\right)^{\gamma-1}=\frac{T}{T_B}$$

$$=1-\frac{\rho_B}{P_B}\cdot\frac{\gamma-1}{\gamma}\cdot\frac{r^2-x^2}{6}f'(t),$$

where subscript B refers to values of pressure P, density ρ, and temperature T at the flame

[17] Following paper, p. 665.

[18] Reference 6, pp. 289–290.

surface and the ordinary symbols to values of these quantities at any point x along radius r of the flame at any time t. γ is the ratio of heat capacities at constant pressure and constant volume. It is seen that at a given instant the temperature, density, and pressure decrease from the flame surface inward and are minima at the center of the sphere. But, as Daniell[19] and Stephenson[20] point out and as Ellis and Morgan themselves realize, the flame speeds are so slow that, according to Bernoulli's theorem, the pressure always must be practically equalized. This must be so whether combustion is complete or not. Avoiding discussion of other difficulties appearing within their derivation concerning the use of the law of adiabatic expansion, we believe that their case for "afterburning" receives no support and that their experimental results simply confirm what is to be expected in the normal course of the combustion process in a closed vessel.

We come now to perhaps the only other experimental facts which might be considered seriously in connection with "afterburning." This interesting experimental work is embodied in a paper by Ellis and Wheeler.[7] The authors made a series of photographs at successive stages during the explosion of carbon monoxide-air mixtures in a glass sphere and cylinder. We believe these very beautiful pictures illustrate not the phenomenon of "afterburning," as the authors proposed, but rather the above phenomenon of the temperature gradient. The photographs show how the inner gas becomes incandescent as soon as the pressure development becomes steep.[21] This is the time at which the temperature of the inner gas begins to rise rapidly due to the compression. It seems unnecessary to resort to any other explanation.

We know of no other published experimental work which conclusively demonstrates the existence of "afterburning." Rather, there appears to be support for the view that the chemical reaction is complete up to equilibrium when maximum pressure is established.

Sharp breaks between the rising pressure curve and the cooling curve, found in fast-burning mixtures, should not exist if there were any appreciable "afterburning." The sharp break indicates abrupt cessation of the chemical reaction. Likewise, in the constant-pressure explosion method in a soap bubble, thousands of explosions carried out by the late Professor F. W. Stevens[22] failed to reveal the slightest indication of further expansion of the burned sphere after the flame had travelled across the entire gas mixture. We are at a loss to reconcile these facts with the hypothesis of "afterburning."

We shall present some other experiments we performed about two years ago, which demonstrate still further the completion of chemical reaction at maximum pressure. The explosions were of stoichiometric mixtures of hydrogen and oxygen and a constant amount of inert monatomic gas, for which we chose helium, argon and mixtures of the two. The initial total pressure was always about 2 atmospheres, and all other conditions were the same. The results, which are given in Table II, show that although the explosion times are different, shortest in the

TABLE II. *Maximum pressures and explosion times in stoichiometric mixtures of hydrogen and oxygen plus equal amounts of helium and argon in varying proportions.*

Mixture ($2H_2+O_2$) plus	Time, sec.	Maximum pressure,* mm deflection
6 A	0.0107	59.8
4 A+2 He	.0100	59.7
3 A+3 He	.00935	60.0
2 A+4 He		60.0
6 He	.00779	59.4
The following set of experiments were made with the film moving at one-fifth the speed of the film in the above set. Times could not be measured accurately but were markedly higher for the helium explosions than for the argon explosions.		
8 A	—	55.9
$5\frac{1}{3}$ A+$2\frac{2}{3}$ He	—	55.9
4 A+4 He	—	55.9
$2\frac{2}{3}$ A+$5\frac{1}{3}$ He	—	55.8
8 He	—	56.0

* The pressures are given in mm deflection of the photographic pressure record.

[19] Daniell, Proc. Roy. Soc. **A126**, 393 (1930).
[20] Stephenson, Trans. Far. Soc. **26**, 577 (1930).
[21] A diagram representing the increase of pressure with the location of the flame front is to be found in the paper by Lewis and von Elbe, reference 16.
[22] Stevens, J. Am. Chem. Soc. **48**, 1896 (1926). National Advisory Committee for Aeronautics paper No. 372, 1930. Also private conferences of the authors with Professor Stevens.

case of straight helium and longest in the case of straight argon, the maximum pressures developed are identical within the limits of measurement. Such results are quite irreconcilable with the viewpoint of "afterburning."

Conclusions

From the foregoing, no cogent arguments appear to have been advanced in favor of "afterburning." It seems to us that the only phenomenon which should receive attention in this connection (but which has not, heretofore) is the effect the temperature gradient in closed-vessel explosions exerts on the maximum pressure. The problem was fully appreciated by Hopkinson as early as 1906.[14a] It is, that due to the temperature dependence of heat capacities of all but monomatic gases, the maximum gas pressure in a closed vessel is lower for unequal than for equal temperature distribution, even though the heat content of the gas is identical in both cases. Thus, establishment of a temperature gradient in closed-vessel explosions prevents attainment of the full pressure and therefore may be considered in a sense analogous to "afterburning." This effect, however, would be independent of the size of the vessel. As to its magnitude, it need only be stated here that it is small, of the order of 0.2 to 0.5 percent in ozone explosions and 0.2 to 0.8 percent in explosions of hydrogen and oxygen with inert gas.[17] Since this difference in pressure is calculable no objections to the explosion method for determining heat capacities can be raised on this account.

Heat-capacity data determined by the explosion method have been called fallacious[23] on account of "afterburning." These objections have now been set aside.

However, in certain types of explosive mixtures there are other phenomena of an entirely different nature, which require careful consideration,[13] for example, lag in the excitation of the vibrational energy levels of the products and the suppression of heat losses by small amounts of water vapor in explosions of hydrogen and oxygen with excess hydrogen.[24]

As far as other criticisms of the explosion method are concerned, we wish to point out that if the requirements of the explosion method are met—and these are a well-designed and properly calibrated pressure indicator, accurate centering of the ignition source, elimination of dead space beyond the exact spherical shape of the vessel, and a volume of vessel large enough to render such disturbances as the ignition rod negligible—accurate heat-capacity data may readily be obtained. In the past the trouble frequently has been failure to meet the above requirements and, on the theoretical side, inadequate dissociation corrections and untenable assumptions regarding heat losses.

It must be admitted that the literature includes many faulty data obtained by this method, but in every case the reason is traceable to one of the causes mentioned. This, for instance, applies to Pier's calculations[4] of his early experiments on the heat capacity of water vapor in which dissociation was neglected; to Bjerrum's estimated heat losses;[24] and to apparent inaccuracies in Siegel's experiments.[24] The facts remain that Pier's original experimental data on hydrogen-oxygen explosions yield, with proper calculations, values of the heat capacity of water which agree with spectroscopic data;[24, 12, 13] that the heats of dissociation of chlorine and hydrogen[25] were determined, which showed reasonable agreement with optical values found later; that our own[26] determinations of the heat capacity and dissociation of oxygen are in excellent agreement with theory; and that our recently determined heat of dissociation of the reaction

$$2H_2O \rightleftharpoons 2OH + H_2$$

as 126,000±2000 calories per 2 mols of H_2O[13] is consistent with Bonhoeffer and Reichardt's[27] value of 128,000±5000 calories determined by an independent method.

[23] See for example, David, Brown and El Din, reference 5; Ellis, Nature **125**, 165 (1930); David, ibid. **129**, 942 (1932).

[24] Wohl and von Elbe, Zeits. f. physik. Chemie **B5**, 241 (1929).

[25] Wohl, Zeits. f. Elektrochemie **30**, 36, 49 (1924).

[26] Lewis and von Elbe, J. Am. Chem. Soc. **55**, 511 (1933).

[27] Bonhoeffer and Reichardt, Zeits. f. physik. Chemie **A139**, 75 (1928).

The Effect of Unequal Temperature Distribution on the Maximum Pressure Developed in Explosions in a Closed Vessel[1]

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When a combustible gas mixture is exploded at the center of a spherical vessel, a temperature gradient is established at the moment of maximum pressure which rises from the wall to the center. The maximum pressure recorded is lower than would have been found had the temperature been equalized without heat loss. A method for calculating this difference in pressure is described. For ozone explosions it is shown to be less than 0.2 percent in weak mixtures and less than 0.5 percent in rich mixtures. For explosions of H_2 and O_2 with inert gases it amounts to 0.2 to 0.8 percent.

WHEN a combustible gas mixture is exploded in a closed vessel a temperature gradient is established which rises from the portion of gas last burned to the point of ignition.[4] The maximum pressure recorded in such an explosion frequently is used to determine the average temperature of the exploded gas by means of the gas law, under the assumption that the maximum pressure is the same, whether a temperature gradient exists or not. Hopkinson[5] recognized that this would be justified only if heat capacities did not change with temperature, but since heat capacities of the products of explosions vary with temperature the maximum pressure recorded is always lower than would have been recorded had the temperature been equalized without heat loss, because the thermal expansion in the hotter parts does not suffice to offset the thermal contraction in the colder parts. Although Hopkinson had no knowledge of the magnitude of this effect he suggested that possibly it was sufficiently large to affect heat-capacity determinations appreciably.[6]

In view of the bearing of this question on the explosion method for determining heat capacities we have calculated the difference between the maximum pressures in the unequalized and equalized temperature states for the explosion of ozone-oxygen mixtures which were used to determine the heat capacity of oxygen.[7] We find that for weak mixtures the difference amounts to less than 0.2 percent, and for the strongest mixtures to less than 0.5 percent. These differences are small enough to leave the previously determined heat capacity of oxygen essentially unaltered. Similar calculations for mixtures of hydrogen and oxygen containing inert gases show a pressure difference of 0.2 to 0.8 percent depending on the composition. Since the difference can be calculated it does not constitute an objection to the explosion method.

Method of Calculation

The method will be outlined for the simplest case, namely, ozone explosions.

The total energy released in an ozone-oxygen explosion is 34,220 calories per mole of ozone at 300° abs. This energy must equal the energy received by all the oxygen molecules after the explosion. If the original mixture contains m moles of oxygen per mole of ozone then $(1.5+m)$ moles of oxygen are present after the explosion. Thus

$$34{,}220=(1.5+m)\left|C_{vD}\right|_{300}^{T_2}\times(T_2-300), \qquad (1)$$

where T_2 is the temperature of the gas in the equalized temperature state and $|C_{vD}|_{300}^{T_2}$ is the mean heat capacity of oxygen at constant volume between 300° and T_2 and is composed of the molecular part of the heat capacity and the part arising from dissociation into oxygen atoms.

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)
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[4] See preceding paper.
[5] Hopkinson, Proc. Roy. Soc. **A77**, 387 (1906).
[6] Compare also Partington and Shilling, *Specific Heats of Gases*, p. 119, 1924.
[7] Lewis and von Elbe, J. Am. Chem. Soc. **55**, 511 (1933).

with mean heat capacities between absolute zero and T_e. Eq. (1) then becomes

$$34{,}220+(1.5+m)\left|C_v\right|_0^{300}\times 300 = (1.5+m)\left|C_{vD}\right|_0^{T_e}\times T_e, \quad (2)$$

where $|C_v|_0^{300}$ is the heat capacity of oxygen between 0° and 300° abs.

For the unequalized temperature state the energies in all elementary fractions, dn, of the gas content of the vessel must be summed up. In the case of a spherical vessel with central ignition this fraction dn is contained in an annular shell at the boundary of a sphere whose gas content is the fraction n of the total contents of the vessel. Hence,

$$34{,}220+(1.5+m)\left|C_v\right|_0^{300}\times 300 = (1.5+m)\int_0^1\left|C_{vD}\right|_0^{T_e}\times T_e dn, \quad (3)$$

where T_e is the temperature within the elementary fraction dn. n varies from 0 to 1.

Knowing the values of the various products $|C_{vD}|_0^{T_e}\times T_e$ as a function of n (see below) and the dependence of heat capacity on temperature, one obtains $|C_{vD}|_0^{T_e}$ and T_e as functions of n and hence the numerical value of

$$\int_0^1 T_e dn.$$

From the gas law $$\frac{P_e}{P_e'}=\frac{(1+\bar{x})T_e}{\int_0^1(1+x)T_e dn}, \quad (4)$$

where P_e and P_e' are the maximum pressures for the equalized and unequalized temperature states, respectively (P_e' is the maximum pressure actually recorded), $\bar{x}$ is the degree of dissociation for the equalized temperature state and x the degrees of dissociation for the various elementary fractions dn (in which the temperatures are T_e) for the unequalized temperature state.

Since it is the ratio of the temperatures before and after temperature equalization that is of interest, even moderately accurate data of heat capacities furnish a quite accurate ratio of P_e/P_e'.

In order to carry out the calculations it is necessary to know the heat capacity of oxygen at various temperatures, the degree of dissociation into atoms at various temperatures and pressures, and the temperature distribution within the vessel at the moment of maximum pressure.

Results

The mean heat capacity of oxygen molecules between 0° and T° abs. was obtained from a former work[7] and is given in Table I.

Table I. *Mean heat capacity of O_2 between 0° and T° abs.*

T° abs.	$\left\|C_v\right\|_0^T$	T° abs.	$\left\|C_v\right\|_0^T$
1400	5.821	2400	6.381
1600	5.949	2600	6.474
1800	6.068	2800	6.554
2000	6.177	3000	6.630
2200	6.279		

$|C_{vD}|_0^{T_e}$ is given by

$$|C_{vD}|_0^{T_e}=|C_v|_0^{T_e}+(\Delta E_T/T)x, \quad (5)$$

where ΔE_T is the heat of dissociation at the temperature T and x is the degree of dissociation. Due to the small change in ΔE_T with temperature and the smallness of dissociation up to 3000°K, ΔE_T may be assumed constant and equal to 116,100 calories per mol without appreciably affecting the final result. x is derived from the equation

$$K_p=[4x^2/(1-x^2)]P_e'. \quad (6)$$

Values for K_p were obtained from a former work.[8]

Calculations were made for two explosions, namely, explosion 2 : 09 where $m=1.497$ and explosion 3 : 32 where $m=1.016$. The latter explosion represents one of our highest temperature explosions.

For both explosions, curves of $|C_{vD}|_0^{T_e}\times T_e$ were drawn against T_e. These curves vary somewhat because the maximum pressures in the two explosions were not the same and the part due to dissociation is different for different pressures.

It may be recalled[9] that at any pressure P during the explosion, the mass element just burned reaches a temperature T_b which may be

[8] von Elbe and Lewis, J. Am. Chem. Soc. **55**, 507 (1933). See also Johnston and Walker, ibid. **55**, 187 (1933).
[9] Lewis and von Elbe, J. Chem. Phys. **2**, 283 (1934).

calculated from known thermal data. This mass element subsequently is compressed adiabatically to pressure P_e' and temperature T_e. Hence

$$T_e = T_b(P/P_e')^{(\gamma-1)/\gamma}, \qquad (7)$$

where γ is the ratio of the mean heat capacity of oxygen between T_b and T_e at constant pressure and constant volume. Knowing T_b, P and P_e', values of T_e can be avaluated by the method of trial and error until the proper value of γ between T_b and T_e is found. Mean heat capacities for these temperature intervals may readily be calculated from the $|C_{vD}|_0^{T_e} \times T_e$ *versus* T_e curve.

The temperature T_e at the boundary of a sphere containing the fraction n of the total contents of the vessel may be calculated by combining Eq. (7) with Eq. (8).

$$n = (P - P_i)/(P_e' - P_i) \qquad (8)$$

Eq. (8) is a simplification of Eq. (2) reference 9.[10]

The integral of Eq. (3)

$$\int_0^1 \left| C_{vD} \right|_0^{T_e} \times T_e dn$$

may now be plotted and evaluated by graphic integration. This value must agree with the value calculated from Eq. (3). $|C_v|_0^{300}$ equals $(5/2)R$ or 4.97 calories per mol.

The difference between the integrated value and the calculated value was found to be small, about 0.25 percent. This constitutes a check on the calculations. A slight adjustment of the plotted curves was made to fulfill Eq. (3) exactly. In Fig. 1, this curve has been plotted for explosion 3 : 32. The area below the curve represents the integral in Eq. (3) and equals the area below the horizontal line, the ordinate of which is the value calculated from Eq. (3), namely, 15,100 calories. From this adjusted curve one obtains values of $|C_{vD}|_0^{T_e} \times T_e$ for various values of n from 0 to 1. From the latter products one obtains values of $|C_{vD}|_0^{T_e}$ and T_e as functions of n.

T_e is now plotted against n and the curve integrated graphically. This gives the value of the integral $\int_0^1 T_e dn$. Similarly, values of the products xT_e are plotted against n and the curve integrated, giving the value of the integral $\int_0^1 xT_e dn$. The sum of these two integrals is the denominator of the right-hand side of Eq. (4). $|C_{vD}|_0^{T_{\bar{e}}} \times T_{\bar{e}}$ and, therefore, $T_{\bar{e}}$ is determined directly from Eq. (2). Knowing the degree of dissociation $\bar{x}$ at this temperature, the ratio P_e/P_e' may now be evaluated.

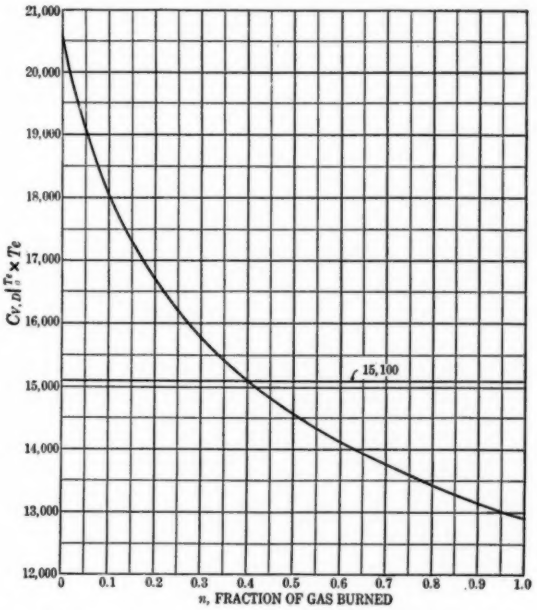

FIG. 1. Plot of product $|CvD|_0^{T_e} \times T_e$ against fraction of gas burned for explosion 3:32.

Table II contains the data of explosion 3 : 32, from which P_e/P_e' was evaluated.

The results of this explosion are

$$\int_0^1 T_e dn = 2339; \quad \int_0^1 xT_e dn = 6.$$

TABLE II. *Heat capacities, temperatures, and degrees of dissociation at maximum pressure for explosion 3:32.* $m = 1.016$; $P_e' = 4814$ mm; $P_i = 492$ mm; $T_i = 301.5°$ abs.; $T_{\bar{e}} = 2353°$ abs.; $\bar{x} = 0.133 \times 10^{-2}$.

n	$\left\|C_{vD}\right\|_0^{T_e} \times T_e$ calories	$\left\|C_{vD}\right\|_0^{T_e}$ calories per mol oxygen	T_e, ° abs.	x, degree of dissociation
0	20,570	7.167	2868	1.440×10^{-2}
0.1	18,050	6.772	2664	0.638
0.2	16,700	6.598	2531	0.357
0.3	15,770	6.486	2431	0.203
0.4	15,100	6.415	2353	0.133
0.5	14,560	6.361	2289	0.095
0.6	14,110	6.320	2232	0.079
0.8	13,440	6.265	2145	0.050
1	12,920	6.222	2069	0.025

[10] This simplification follows from the condition that $n(=v_i/V) = 0$ when $P = P_i$ and from the fact that the denominator of the second term on the right-hand side of Eq. (2), reference 9, is practically constant over the temperature range under consideration.

TABLE III. *Effect of temperature gradient on maximum pressure in hydrogen-oxygen and ozone explosions.*

Explosion No.	138		147		144		153		166		161		29		2.09	
m_{H_2O}	0.169		0.126		0.113		0.835		0.101		0.096		0.108			
m_{H_2}	0.297		0.776		0.546		0.523		4.057		0.443		2.598		$m_{O_2}=1.497$	
m_{N_2}	—		—		—		—		—		3.186		0.012			
m_A	7.23		4.31		3.52		3.095		—		—		—			
	Te	x	Te	x	Te	x	Te	x	Te	x	Te	x	Te	x	Te	x
$m=0$	2622	0.0042	2933	0.0154	3110	0.0258	2775	0.0124	2540	0.0057	2584	0.0046	2924	0.024	2554	0.0048
$=0.2$	2247	.0006	2576	.0037	2787	.0091	2511	.0044	2270	.0016	2310	.0014	2698	.011	2232	.0010
$=0.4$	2042	.0001	2391	.0017	2633	.0051	2360	.0022	2123	.0006	2178	.0005	2560	.006	2068	.0004
$=0.6$	1911	—	2259	.0009	2511	.0030	2247	.0010	2026	.0004	2089	.0001	2459	.004	1960	—
$=1.0$	1743	—	2070	.0002	2323	.0011	2097	.0003	1900	.0001	1950	—	2320	.002	1825	—
$\bar{Te}$	2044		2386		2625		2352		2120		2170		2553		2064	
$\bar{x}$	0.0001		.0017		.0049		.0020		.0006		.0005		.0060		.0004	
Pe/Pe'	1.0064		1.0066		1.0071		1.0052		1.0025		1.0018		1.0034		1.0024	

Therefore, from Eq. (4)

$$P_e/P_e' = (1.00133 \times 2353)/(2339+6) = 1.0047.$$

When explosion 2 : 09 is treated in the same way $P_e/P_e' = 1.0024$.

In the case of hydrogen-oxygen explosions the calculations are very much more complicated[11] because of the dissociation equilibria between H_2, O_2, OH, H and O. In Table III the first six explosions are Pier's,[12] the seventh is Wohl and Magat's[13] and the eighth is Lewis and von Elbe's. m_{H_2O}, m_{H_2}, m_A, etc., are the mols of excess H_2O, H_2 and A in the original mixture per mol of H_2O formed in the explosion.

For explosions 138 to 29

$$x = ((1+m_{H_2O})0.5x_{II} + m_{H_2}x_{H_2})/(1+\Sigma m) \quad (9)$$

where x_{II} is the degree of dissociation of H_2O into OH and H_2 (dissociation into O_2 and H_2 is negligible) and x_{H_2} the degree of dissociation of H_2 into atoms.

[11] Method will be explained in future publication.
[12] Pier, Zeits. f. Elektrochemie **15**, 536 (1909).
[13] Wohl and Magat, Zeits. f. physik. Chemie **B19**, 117 (1932).

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The Third Law of Thermodynamics

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The invariance of statistical weights requires that the entropy of any phase approach zero at 0°K. The uncertainty principle, however, makes it impossible to define a state of absolute zero for a substance whose lowest energy states are closely spaced multiplets.

SOME years ago Lewis and Gibson[1] predicted that the behavior of solutions and undercooled liquids was likely to prove exceptional so far as the third law is concerned. From the practical standpoint, their prediction has been amply confirmed. Furthermore, we learn from spectroscopic evidence that heat effects due to spin orientation are to be expected at temperatures so low that there is no prospect at present of their attainment. The entropy of a substance as calculated from specific heat measurements is, therefore, often subject to a revision from spectroscopic or equilibrium data. This, however, may be regarded as an experimental difficulty. The question of the validity of the third law in an academic sense could not be given a definite answer until the development of wave mechanics. For example, Pauling and Tolman[2] attempted to show that the entropy of a glass was greater than zero at zero Kelvin by considering a process of

[1] Lewis and Gibson, J. Am. Chem. Soc. **42**, 1529 (1920).
[2] Pauling and Tolman, J. Am. Chem. Soc. **47**, 2148 (1925).

reversible evaporation at very low temperature. Such a process would, however, require an indefinitely long time, and, during this time, one could not say what changes were taking place in the glass. It might crystallize, for example. This difficulty foreshadows, in a curious way, the consequences of the uncertainty principle.

Recently Eastman and Milner[3] have investigated experimentally the application of the third law to crystalline solutions, and have given a general discussion of the validity of the third law. Essentially the same conclusion as to the validity of the third law is reached in this paper as in theirs, but they have postulated a distribution of energy states in the crystal which is essentially different from that which is postulated here. It is believed that a more satisfactory picture of the situation is presented in this paper.

In order to picture the conditions under which matter is likely to appear to be an exception to the third law, let us consider a crystalline solution. Assuming it to be an ideal solution, e.g., a mixture of isotopes, then the partial vapor pressures of the constituents in equilibrium with the solution are less than those of the pure crystals, respectively. Hence, there is an increase of entropy on mixing. This decrease in partial vapor pressure is the characteristic thing, and it comes about because in the crystalline solution there is the possibility of different configurations of the same energy. The word "configurations" is here used in the sense prescribed by the Bose-Einstein statistics, in which the interchange of like atoms does not constitute a different configuration. It is important to note that the configurations must all have the same energy.

This statement is not limited to ideal solutions in its application. For an extreme example we may consider a liquid which may be cooled to form a glass. At high temperatures there are many configurations in the liquid having the same energy. By this we mean that, if a quantity of the liquid were held in a constant temperature bath, no observable fluctuations would take place in the energy content of the liquid. As the liquid is cooled, a single configuration of lower energy than any other may appear, but this is the crystalline state. If this state appears the entropy of fusion is lost and the substance no longer shows any peculiarity in behavior so far as the third law is concerned. On the other hand, if a glass is formed then the configuration resulting must be one of a great number, otherwise we should not get reproducible specific heat curves for the undercooled liquid. This does not mean, of course, that there may not be some reduction in the number of configurations with corresponding loss of entropy in forming the glass from the liquid.

Likewise, if one configuration in a crystalline solution had a lower energy than any other, we should have a preferred orientation with the formation of a compound and the loss of the entropy of mixing. The characteristic property of those substances that cause difficulties for the third law is, therefore, the existence of a large number of configurations of the same energy, of which a single one may be "frozen" out by cooling to lower temperatures.

Let us return to the consideration of the ideal crystalline solution. It can be shown from the dynamics of the crystal lattice that such a crystal will not have a heat capacity essentially different from that of the pure crystals so far as "classical" quantum theory is concerned, and hence, the entropy of mixing will persist to low temperatures. It remains to consider what difference is predicted by the wave mechanics.

The behavior to be expected according to the new quantum theory is best exemplified by the simple case of the optical isomers. The dextro and laevo forms of a molecule are configurations of exactly the same energy from the classical viewpoints. According to wave mechanics, however, these molecules do not exist as the simple *d* or *l* forms in a single configuration, but always in states which represent both configurations. The result is that the energy levels of the optical isomers are doublets.[4] Since the transformation of the molecule from the one form to the other involves the traversal of an energy crest, we have molecules existing in one form for long periods of time, but the statistical weight associated with lowest energy state, for example, is double that to be expected on classical theory, and is the same as classical theory would predict, provided the molecule passed readily from one configuration

[3] Eastman and Milner, J. Phys. Chem. **1**, 444 (1933).

[4] These doublets are observed spectroscopically in the ammonia molecule.

to the other. The analogy of the crystalline solution is at once apparent. We have a number of configurations of the same energy separated by energy crests. By linear combinations of symmetric and antisymmetric wave functions, we obtain a total number of wave functions equal to the degeneracy; that is to say, the total number of configurations having the same energy. Thus, instead of each configuration having a distinct energy, each configuration now has a large number of closely spaced energy levels.

If one configuration is cooled to a temperature so low that it is no longer possible for it to traverse the energy crests separating it from the other configurations, its energy levels will have a multiplicity sufficient to maintain the same statistical weight as would exist by the classical theory for all of the configurations. This is the law of invariance of statistical weights.

The separation of these multiple levels is the smaller; the greater, the energy crest separating the configurations. We may see at once, therefore, that there is no likelihood of making a delicate enough measurement to show that this multiplicity of energy levels exists for a crystalline solution.

When we consider the measurement of the small heat effects to be expected as a result of this multiplicity as a theoretical possibility we encounter in a more definite form the same difficulty that was found in connection with the reasoning of Pauling and Tolman referred to above. The energy quantities to be observed are very small. The uncertainty principle requires that their measurement occupy a long time—in fact, a time of the same order of magnitude as is required for one configuration to transform "spontaneously" into another. This means, of course, that we could not be sure that we were measuring the heat capacity of the substance that we started with, and hence, we could prove nothing. We may conclude, therefore, that the statistical weights of any form of matter are such that the entropy should always become zero at zero Kelvin, but only for those substances which reach the lowest energy states well above absolute zero can the statement be demonstrated even by "theoretical" experiment.

Temperatures well below 1°K have been reached in the laboratory, and there is no difficulty in defining as zero the entropy of any substance which reaches its lowest energy state at such temperatures. But for those substances that must be cooled very near to zero Kelvin in order to reach the lowest energy level, the difficulty arises that the absolute zero itself is indeterminate. Instead of the principle of the "unattainability of the absolute zero" we have the uncertainty principle.[3]

A temperature measurement is a measurement of energy, and we could not be sure that a mass of substance was at absolute zero except as a limiting result of observation extended over a long interval of time.

The lowest energy state of a substance such as we are discussing would not be associated with any particular configuration. This means, in common sense language, that by the time we had determined the substance to be in the lowest state, the configuration existing would probably be different from the one with which we started.

There is no reason to suppose, as has been suggested,[5] that two isomers, such as methyl ether and ethyl alcohol, do not combine, but even if the two had exactly the same energies the doublet separation would be too small to be observed experimentally. In principle, of course, this situation would lead to an indeterminacy in the entropy, just as the cases discussed above. But practically there can be no difficulty in defining the entropy of a pure substance.

The foregoing considerations have been applied to the ideal crystalline solution, but they may be applied to any crystalline solution or glass without essential change. The case of liquid helium is, perhaps, unique because the entropy of the liquid is near zero at temperatures attainable in the laboratory. Here one might suggest that the number of different configurations is not large, and that the energy crests are small, so that the multiplet separation is appreciable. It must be remembered, however, that the reason helium does not form a crystal is that the zero-point energy exceeds the bonding energy of the crystal lattice. For this reason, liquid helium at low temperatures may be considered to be in a state resembling very closely the crystalline state with a very definite zero-point energy.

[5] Mayer, Brinauer and Mayer, J. Am. Chem. Soc. **55**, 37 (1933).

The Significance of Chemical Bond Energies

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In view of recently reported departures from bond additivity of chemical energies of formation, a purely empirical study has been made of the significance of chemical bond energies. If one assumes that the energy of formation is made up of bond energies and interaction energies between the bonds as well, it is shown that both of these two types of energy are *indeterminate* so far as thermochemical data are concerned. Under certain simple conditions on the interaction energies *apparent* bond additivity would obtain and one could then define apparent bond energies. In case these additivity conditions are not valid, it is further shown how the energy of formation can be expressed in terms of the apparent bond energies with a correction term involving the numerical departures from the additivity conditions. It is also shown that under a transformation of reference state to excited states of the atoms: (1) the additivity characteristics are invariant, and (2) the bond resonance energies as defined by Pauling are invariant, and therefore the reference of bond energies to excited states has no significance so far as these resonance energies are concerned. A discussion of atomic and bond additivity is given for physical quantities in general. It is pointed out that the energy connected with the nuclear motions, that is the heat content plus the zero-point energies of the vibrations, may be of the order of one-tenth the total energy of formation. Since this latter energy would not be expected on the whole to exhibit bond regularities, it is therefore proposed that "electronic" energies be introduced for the study of structural regularities in the energies of formation. A study is then made of available data in terms of the proposed scheme. Because of the lack of accurate data it is at present not possible to make a very thorough test. But a certain amount of information is obtained from the excellent data of Rossini on some of the CHO compounds, and so far as reliable data are available reasonable results are obtained, which indicate that in some cases the departures from additivity may be considerably greater than ordinarily supposed. It is further pointed out that Pauling's bond resonance energies could not accurately be considered as pure bond quantities if the interactions were appreciable, and that this may be the reason in part, that his electronegativity map cannot on the whole be used successfully to predict the electric moments of chemical bonds.

SINCE considerable importance is attached to bond energies in theoretical chemistry, and since there seems to be some arbitrariness in their definition, it was thought worth while to consider in a somewhat general manner what empirical inferences one is justified in making on the basis of experimentally determined heats of formation. It is a well-known fact that the energies of formation of molecules from their atomic constituents can approximately be accounted for on the assumption that each chemical bond type has associated with it a characteristic energy in the sense that the bond energies are additive. Some of the arguments of theoretical chemistry are based on the general validity of this principle. For example, it has sometimes been rather naturally inferred from the empirical facts, that each chemical bond has associated with it a definite electronic configuration, independent of the other bonds to the same atom.

Actually departures from additivity are observed and usually attributed to experimental error or to "dipole effects." For example, it is well known that the C—C bond energy calculated from the paraffins is about 0.2 v.e. less than that obtained from the diamond crystal. Also Rossini[1] has recently reported a discrepancy of about 0.3 v.e. for the paraffins and alcohols, and Pauling[2] has mentioned a discrepancy of 0.3–0.5 v.e. for the primary and branched alcohols. For the purpose of studying such deviations empirically it is proposed to consider the consequences of assuming a more general type of energy model, which admits the possibility of "bond interactions." To be more precise, it will be assumed as a second approximation, that the energy of formation of a molecule may be considered to consist of a set of energies associated with the "bonds" and an additional set associated with "pairs of bonds" to the same atom.

For the sake of generality it will be convenient to consider not necessarily a single molecular type, but a more generalized system of atoms connected in any of the various ways allowed by the valence conditions. The discussion will for the present be further restricted to saturated

[1] F. D. Rossini, J. Chem. Phys. **2**, 145 (1934).
[2] L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

systems, containing only single bonds. (Such a model would be expected to apply only when the valence angles of the individual atoms are all equal, or nearly equal, as for valencies up to four; and only when the interactions between atoms not bound to a common atom are negligible.)

There will be associated with the bond between the atoms X_i and X_j an energy R_{ij}; and with the pair of bonds X_i-X_j and $X_i-X_{j'}$ to the atom X_i, an energy $R^i_{jj'}$. The energy of the system of molecules can then be written:

$$E=\sum_{ij}^{\text{bonds}} R_{ij}+\sum_{i}^{\text{atoms}}\sum_{j,\,j'}^{\text{pairs}} R^i_{jj'}.$$

One may then ask the following question. Are there any possible conditions on the $R^i_{jj'}$ such that the second, or double summation term of E could be expressed in the form of a single summation term like the first term, independent of the number of like bonds in the system? That is, are there any simple conditions on the interaction constants, such that the interaction energy would be experimentally indistinguishable from the bond energy, so far as E is concerned?

It can be shown as follows that the conditions:

$$R^i_{jj'}-(R^i_{jj}/2+R^i_{j'j'}/2)=0 \qquad (1)$$

are *sufficient* conditions for apparent bond additivity: If the atom X_i has the valence v_i, there will be $v_i(v_i-1)/2$ terms of the type $R^i_{jj'}$ associated with the atom X_i, and each quantity $R^i_{jj}/2$ will occur (v_i-1) times in the summation over the atoms X_i, when the substitution (1) is made. Hence one can write:

$$\sum_{j,\,j'}^{\text{pairs}} R^i_{jj'}=\sum_{ij}^{\text{bonds}} \tfrac{1}{2}(v_i-1)R^i_{jj}.$$

This shows that the atoms X_i and X_j may be considered to contribute additional energies

$\frac{1}{2}(v_i-1)R^i_{jj}$ and $\frac{1}{2}(v_j-1)R^j_{ii}$, respectively,

to the bond energy R_{ij}, independent of the numbers of bonds of the various types present. One can then write:

$$E=\sum_{ij}^{\text{bond types}} N_{ij}E_{ij},$$

where

$$E_{ij}=R_{ij}+\tfrac{1}{2}(v_i-1)R^i_{jj}+\tfrac{1}{2}(v_j-1)R^j_{ii}$$

and N_{ij} is the number of bonds ij in the system. The quantities E_{ij} may be called the apparent bond energies. Thus one sees that a sufficient condition for apparent bond additivity is the simple condition that the interaction energy between two unlike bonds to the same atom be equal to the average of those for the two corresponding pairs of like bonds,—with no restriction on the order of magnitude of the interaction energies! For example, a special case of this condition would obtain if all the interactions were equal to one another.

It can further be shown that the conditions (1) are also necessary conditions for bond additivity of the type previously discussed. Since the proof is somewhat lengthy and of only mathematical interest, it is not included here. It is a simple matter to prove it for any special types of compound.

One can also enquire under what conditions a given system of bond energies designated by S_{ij} may equally well be interpreted formally as interaction energies $S^i_{jj'}$. In terms of the energies S_{ij} one can *always* define a system of energies $S^i_{jj'}$, in fact by the following equations:

$$\begin{cases} S_{ij}=\frac{1}{2}(v_i-1)S^i_{jj}+\frac{1}{2}(v_j-1)S^j_{ii}, & (i\neq j)\\ S_{ii}=(v_i-1)S^i_{ii},\\ S_{jj}=(v_j-1)S^j_{jj},\\ S^i_{ij}=S^i_{ii}/2+S^i_{jj}/2,\\ S^j_{ij}=S^j_{ii}/2+S^j_{jj}/2. \end{cases}$$

For an aggregate of only two types of atoms, X_i and X_j, these equations will represent a system of only five equations in the six quantities $S^i_{jj'}$ to be defined. The two quantities S^i_{ii} and S^j_{jj} are uniquely defined. Therefore any one of the other four of these interaction constants is completely arbitrary, and it will be possible always to represent a system S_{ij} formally in terms of an equivalent system $S^i_{jj'}$ in a single infinity of different ways. For a system of n atomic types there will be $n(n-1)/2$ degrees of arbitrariness in the choice of interaction constants.

This arbitrariness can be expressed in another way; namely, by considering the set of bond energies defined by $T_{ij}=0$, and calculating the equivalent $T^i_{jj'}$, as the $S^i_{jj'}$ previously. Hence it

is always possible to add to a system of bond energies R_{ij} a system of interaction energies of the type $T^i_{jj'}$ without changing the total energy E. This system of energies will, of course, have the same degree of arbitrariness as the system $S^i_{jj'}$.

Departures from Apparent Bond Additivity

In the above discussion it has been stated that the necessary and sufficient conditions for apparent bond additivity are given by the Eqs. (1). If these latter conditions are not valid, one may write:

$$R^i_{jj'}-(R^i_{jj}/2+R^i_{j'j'}/2)=\delta^i_{jj'}, \qquad (2)$$

where it may be noted that the $\delta^i_{jj'}$ differ from zero only when $j\neq j'$. With the use of Eqs. (2) the total energy may be rewritten:

$$E=\sum_{ij}^{\text{bond types}} N_{ij}R_{ij}+\sum_{i}^{\text{atoms}}\sum_{j,\,j'}^{\text{pairs}} \times\{\tfrac{1}{2}(R^i_{jj}+R^i_{j'j'})+\delta^i_{jj'}\}.$$

And if it be noted that the quantities

$$\tfrac{1}{2}(R^i_{jj}+R^i_{j'j'})$$

represent a system of energies obeying the transformation conditions (1), then one can write:

$$E=\sum_{ij}^{\text{bond types}} N_{ij}E_{ij}+\sum_{i}^{\text{atoms}}\sum_{j,\,j'}^{\text{pairs}}\delta^i_{jj'}, \qquad (3)$$

where the E_{ij} have the same form as in the previous case of perfect additivity. In addition there is here a correction term to be summed over all pairs ($^i_{jj'}$) for which $j\neq j'$. The correction term will depend not only on the numbers of bonds N_{ij} and the numbers of atoms N_i, but also on the manner in which the atoms are connected. For example different isomers may have different correction terms. In order to specify the connections of the generalized system under consideration, one can imagine various subtypes of the atoms X_i according to the particular set of atoms $X_{j_1}\cdots X_{j_{v_i}}$ to which the atom X_i is bound. These subtypes may be symbolized by: $X_i{}^{j_1\cdots j_{v_i}}$ and their frequency of occurence in the system by: $N_i{}^{j_1\cdots j_{v_i}}$. For the purposes of the present discussion, the system is then completely specified by these latter numbers. The correction term can be expressed as:

$$\sum_{i,\,jj'}^{\text{pair types}} p^i_{jj'}\delta^i_{jj'},$$

where the $p^i_{jj'}$ represent the total number of interactions of the type $R^i_{jj'}$ in the system, and are expressed by linear forms, with integral coefficients, in the $N_i{}^{j_1\cdots j_{v_i}}$. They may be regarded as characteristic indices for the system or molecule as regards bond additivity. They do not include the particular $N_i{}^{j_1\cdots j_{v_i}}$ for which the j's are all identical.

When departures from additivity are admitted, it is, of course, arbitrary how one defines bond energies, because one can always apply appropriate correction terms. But since the above analysis suggests a simple and natural definition, it will be used as an empirical basis for the discussion of thermochemical data. If one restricts oneself to particular types of compound, it may be possible in some special cases to obtain apparent additivity, but if one *assumes* additivity for a particular set of compounds and calculates appropriate bond energies, one does this in general at the expense of having to ignore discrepancies in other compounds. This is illustrated by the previously mentioned discrepancies, and by still other fairly large discrepancies, which seem to appear consistently for the first members of homologous series and are usually ignored by taking an average for the series.

In addition to offering a possible explanation for the observed discrepancies, the above analysis leads to the significant conclusion, that thermochemical data alone can offer no possibility of distinguishing between interaction energy and bond energy in the usual sense. In the case of perfect apparent additivity it is impossible to obtain any information whatsoever concerning the relative amounts of the two types of energy. Even in the case of departures from additivity, with the model considered here, it would at most be possible to obtain from the observed $\delta^i_{jj'}$ a lower limit for the absolute values of the largest $R^i_{jj'}$.

Reference of Bond Energies to Excited States

Bond energies have sometimes been referred to excited states of the constituent atoms. For example, Pauling has calculated bond energies referred to the ^5S state of the carbon atom, because the tetravalent carbon atom has been supposed to be closely related to this latter state of the atom. With reference to the present treatment one can consider what significance such a reference to excited states could have on the basis of thermochemical data alone. It will be supposed that the energy E referred to normal atoms is given by Eq. (3). If one wishes to refer the energy of formation to excited states, it is obvious that this energy will be increased by an amount

$$\sum_{i}^{\text{atoms}} N_i\epsilon_i,$$

where N_i is as before the number of atoms X_i in the system, and ϵ_i is the excitation energy of the atom X_i relative to the normal state. Now one can imagine the energy ϵ_i to be divided equally between the v_i bonds to the atom X_i, and then write:

$$E=\sum_{ij}^{\text{bond types}} N_{ij}(E_{ij}+\epsilon_i/v_i+\epsilon_j/v_j)+\sum_{i,\,jj'}^{\text{pairs}} p^i{}_{jj'}\delta^i{}_{jj'}.$$

Hence it is seen that the characteristic apparent bond energies are increased, but that the additivity correction remains invariant under such a transformation. From this it can be inferred not only that perfect additivity would not be altered by such a transformation, a well-known fact, but also that the quantities $\delta^i{}_{jj'}$ obtained from heats of formation would be invariant to the particular choice of reference states.

Pauling's Bond Resonance Energies

With regard to this transformation one can make a further inference concerning the resonance energy of a bond as calculated by Pauling. These resonance energies were defined by:

$$\Delta_{ij}=E_{ij}-\tfrac{1}{2}(E_{ii}+E_{jj})$$

and calculated on the assumption of perfect additivity. They are supposed to represent the resonance energy between a "normal covalent bond" and the ionic bond. If the E_{ij} are referred to normal states, then the $E^*{}_{ij}$ referred to excited states will be given by: $E^*{}_{ij}=E_{ij}+\epsilon_i/v_i+\epsilon_j/v_j$, whence it is immediately obvious that $\Delta^*{}_{ij}=\Delta_{ij}$. In other words, the resonance energies calculated on the assumption of perfect additivity for a particular set of compounds will be invariant to the transformation from normal to excited states. It will vary somewhat with the choice of compounds, corresponding to the departures from additivity.

When one admits departures from additivity, or even when one admits interactions obeying the additivity requirement (1), it is a difficult question as to what one should consider a "normal covalent bond" in the sense of Pauling's calculations. So far as the empirical calculations for an electronegativity map are concerned, it might seem just as well to calculate resonance energies in terms of the apparent bond energies E_{ij} as defined in the present analysis. But a simple calculation of the resonance energies shows that they are not independent of the interactions except under very special conditions.

Calculation of the Interaction Increments

Considering again the "interaction increments," $\delta^i{}_{jj'}$, it is evident that one should be able to calculate them directly from the thermochemical data without calculating energies of formation at all, since they are invariant under a transformation to excited states. Energies of formation are most frequently calculated from experimental heats of combustion. The energy of formation is then given by a linear equation in the numbers N_i:

$$E=\sum_{i}^{\text{atom types}} N_i\mu_i-(K+\lambda).$$

The quantities μ_i are constants derived from the auxiliary thermochemical reactions involved, and depend on the particular atomic states of reference. K is the heat of combustion measured in any physical state; and λ, the heat of vaporization from the same state. It will be supposed that the calculations are referred to normal atoms. Then the energy of formation can be expressed also in the form (3). Combining the two ex-

pressions for the energy of formation one can eliminate E and write:

$$-(K+\lambda)=\sum_{ij}^{\text{bond types}} N_{ij}(E_{ij}-\epsilon_i/v_i-\epsilon_j/v_j) + \sum_{i,\,jj'} p^i{}_{jj'}\delta^i{}_{jj'}.$$

This shows that the negative quantities $-(K+\lambda)$ have the same bond additivity characteristics as the energies of formation E. Hence one could calculate the $\delta^i{}_{jj'}$ directly from the experimental quantities. In fact one does not even need to specify the μ_i since the quantities in parentheses will be determined from the data without a knowlege of their constitution, and are themselves invariant to the choice of reference. But since it is useful to determine energies of formation and bond energies, this latter method will not be used in the subsequent applications. The actual energies will be calculated with reference to normal states, since the foregoing discussion has shown that the introduction of excited states has no special significance for the present considerations.

Atomic Additivity

From the previous discussion of excited states, it is obvious that an additive system of any "atomic" physical quantities R_i can always be replaced by an additive system of bond quantities R_{ij} defined by:

$$R_{ij}=R_i/v_i+R_j/v_j.$$

These equations define the R_{ij} uniquely. The reverse transformation will be possible when

$$\Delta_{ij}=R_{ij}-(R_{ii}/2+R_{jj}/2)=0.$$

If this latter condition does not hold the corresponding quantity E can be written:

$$E=\sum_{i}^{\text{atoms}} \tfrac{1}{2}v_iR_{ii}+\sum_{ij}^{\text{bonds}} \Delta_{ij}.$$

From the foregoing one sees that the condition that bond quantities R_{ij} be representable as atomic quantities R_i is simply that the quantities Δ_{ij}, similar in form to the resonance energies defined by Pauling, should vanish; whereas the condition that interaction quantities $R^i{}_{jj'}$ be representable as bond quantities R_{ij} was seen to be simply that the quantities $\delta^i{}_{jj'}$ should vanish. As regards additivity then the Δ_{ij} might be regarded as characterizing an abnormality in the interactions associated with conventional bonds; and the $\delta^i{}_{jj'}$, an abnormality in the interactions between atoms not bound to each other but to the same atom, X_i.

One can summarize the above results by stating the following general additivity rules:

(I) An additive system of atomic quantities can always be replaced by an additive system of bond quantities R_{ij}, uniquely defined as above. The reverse transformation will be possible when the Δ_{ij} vanish.

(II) An additive system of bond quantities R_{ij} can always be replaced by an additive system of interaction quantities $R^i{}_{jj'}$ in an infinite variety of ways as previously defined. The reverse transformation will be possible when the $\delta^i{}_{jj'}$ vanish.

These principles have a number of obvious consequences, the most significant of which is the following. If for the sake of argument one admits purely formally the possibility of atomic bond an interaction energies, it is impossible from the experimental energies E to assign unique quantities R_i, R_{ij} and $R^i{}_{jj'}$ to the different types of atoms, bonds and interactions, respectively. So far as energies are concerned, it is therefore impossible to justify unambiguously the use of such terms as atomic, bond, and interaction energies. In fact, the only quantities uniquely determinable form the energies of formation are the invariant quantites Δ_{ij} and $\delta^i{}_{jj'}$. While the consideration of atomic energies has no special significance here, except in the formal transformation to excited states, the latter discussion was included for the sake of generality and because of its possible interest for empirical studies of refractivity and other physical quantities.

It is perhaps worth repeating here that the present discussion represents an attempt to determine only the purely empirical significance of chemical bond energies. This discussion has shown that apparent bond additivity does not, as frequently inferred, necessarily permit the assignment of characteristic energies to chemical bonds

disregarding the possibility of interactions. No attempt is made here to discuss bond and interaction energies from the point of view of an extended quantum analysis. Such an analysis is promised from the studies of Van Vleck and his students.

Applications

In order to determine the quantities $\delta^i_{jj'}$ from experimental data it is first necessary to determine the indices $p^i_{jj'}$ for the various compounds to be considered. These can be determined by directly counting the number of interactions of the type $R^i_{jj'}$ in the molecule; but it is sometimes more convenient to express them in terms of the characteristic subtype numbers previously introduced. In Table I are shown the

Table I. *Subtypes in CHO compounds.*

C_{CCCC} n_0	C_{CCCH} n_1	C_{CCHH} n_2	C_{CHHH} n_3	C_{HHHH} n_4
	C_{CCCO} n_1'	C_{CCHO} n_2'	C_{CHHO} n_3'	C_{HHHO} n_4'
		C_{CCOO} n_2''	C_{CHOO} n_3''	C_{HHOO} n_4''
			C_{COOO} n_3'''	C_{HOOO} n_4'''
				C_{OOOO} n_4''''
O_{OO} m_0	O_{OC} m_1	O_{CC} m_2	H_H r_0	H_C r_1
	O_{OH} m_1'	O_{CH} m_2'		H_O r_1'
		O_{HH} m_2''		

$$\begin{cases} p^C{}_{CH}=3n_1+4n_2+3n_3+2n_2'+2n_3'+n_3'' \\ p^C{}_{CO}=3n_1'+2n_2'+n_3'+4n_2''+2n_3''+3n_3''' \\ p^C{}_{OH}=n_2'+2n_3'+3n_4'+2n_3''+4n_4''+3n_4''' \\ p^O{}_{CH}=m_2' \\ p^O{}_{CO}=m_1 \\ p^O{}_{OH}=m_1' \end{cases}$$

various possible subtypes for CHO compounds (compounds of carbon, hydrogen and oxygen containing only single bonds), together with new and simpler symbols to designate their frequency of occurence in the molecule. Expressions for the six different $p^i_{jj'}$ are also given.

It is a characteristic of the $p^i_{jj'}$ that the group numbers n, m or r corresponding to groups for which all the surrounding atoms are alike (e.g., C_{CCCC} or C_{HHHH}) never occur. Therefore the correction term vanishes for compounds made up of such groups alone, and one can obtain the apparent bond energies from compounds of the latter type, if they exist. In these cases then the bond energies can be calculated as in the case of perfect additivity. For the particular case of CHO compounds the molecules H_2, H_2O, CH_4, and the diamond crystal (neglecting surface effects) are compounds of the latter type. The energies of formation of these compounds serve to determine the bond energies E_{HH}, E_{OH}, E_{CH}, and E_{CC}, respectively. Compounds containing only C_{OOOO} or O_{CC} groups are not known, and the energy E_{CO} must be determined indirectly. The possibility that O_4 is made up of O_{OO} groups with normal bonds will be discussed later in connection with the determination of the bond energy E_{OO}.

CH Compounds

As a special case of CHO compounds one can consider CH compounds, including all the paraffins, diamond and hydrogen, H_2. There will be just four constants to be determined from the experimental data; namely, E_{CC}, E_{CH}, E_{HH}, and $\delta^C{}_{CH}$. In principle it would seem a fairly simple matter to test the present point of view by means of a study of the energies of formation of the paraffins. The bond energy E_{CC} would be obtained from the diamond crystal; and E_{CH}, from methane. Then the values of $\delta^C{}_{CH}$ as calculated from the different paraffins should all be the same.

But if one attempts to make an accurate study of thermochemical data, several difficulties are encountered:

(1) Thermochemical data, such as heats of combustion, seem in very few cases to have been determined with an accuracy better than 0.1 v.e. Of the older data Thomsen's values seem to be fairly reliable, as judged from the agreement with more recent data. For a few organic compounds Rossini[3] has recently made some excellent measurements of the heat of combustion.

[3] F. D. Rossini, Bur. Standards J. Research **6**, 1, 37 (1931); **7**, 329 (1932); and **8**, 119 (1933).

(2) It is customary to calculate energies of formation of the molecule from the isolated elements at a temperature of 20°C. The heat of combustion is usually determined at this latter temperature approximately, and if the substance is not burned from the gaseous state, it is necessary to know the heat of vaporization at 20°C. Since one usually finds in the literature the heat of vaporization at the boiling point, for example, a knowledge may be required of the specific heat of the liquid, or solid, and of the vapor for temperatures from 20°C to the boiling point, or to the point at which the sublimation energy has been determined. Sometimes these data are available, but more frequently they are not, and one must make an estimate subject to appreciable error in some cases.

(3) Added to these there is a more fundamental difficulty: The conventional energies of formation give the total energy of the molecule at 20°C. This energy may be regarded as made up of an electronic and a nuclear energy of opposite sign associated with the nuclear motions and their corresponding potential energy. One part of this nuclear energy will consist of the heat content of the gas per molecule, and another part will be the sum of the zero-point energies of the fundamental modes of nuclear vibration. The zero-point energy is in general much larger than the heat content at 20°C. For example, the zero-point energy corresponding to a frequency of 3000 cm^{-1} is about 0.2 v.e., while the heat content per degree of freedom on the equipartition theory, $\frac{1}{2}kT$, is only about 0.01 v.e., and unless the frequency is very low only a small fraction of the classical energy is excited. So far as the order of magnitude of the frequencies is concerned there seems to be in general one mode of vibration which may be imagined to be associated roughly with each chemical bond. Besides these "valence" frequencies there are usually many other frequencies associated with deformation or free rotation. Therefore one does not expect the nuclear energy to exhibit bond additivity. In fact, it seems surprising that approximate bond additivity has been observed at all. In view of these considerations one would expect at most that the electronic energy might show structural regularities. It is therefore proposed in the following to introduce electronic energies of formation. These energies will be greater (arithmetically) than the ordinary energies by an amount equal to the nuclear energy. They will, of course, not correspond to an actual state of the molecule, but will be analogous to the energy of a diatomic molecule corresponding to the theoretical minimum of potential energy.

One might suggest that the observed departures from additivity could possibly be accounted for entirely in terms of the nuclear energies, but as will be seen in the following, it seems to be necessary to introduce some additional feature into the energy model in order to correlate empirically the observed energies of formation. In the following an attempt will therefore be made to correlate existing data in terms of the interaction increments $\delta^{i}_{jj'}$.

Because of the lack of accurate experimental data it is at present not possible to make a very thorough test of the present point of view; but some information can be obtained from data on CHO compounds, particularly from the excellent data of Rossini. In Table II are given the constants of the auxiliary reactions used in the calculations. These lead to the following equation for the heat of formation in v.e. of CHO compounds of the type discussed here:

TABLE II.

$2O = O_2 + 5.09$ v.e.
$2H = H_2 + 4.44$ v.e.
$H_2 + \frac{1}{2}O_2 = H_2O(g) + 2.508$ v.e.
$H_2 + \frac{1}{2}O_2 = H_2O(l) + 2.966$ v.e.
$C(g) = C_{graphite} + 6.67$ v.e.
$C_{graphite} + O_2 = CO_2 + 4.075$ v.e.
$C_{graphite} = C_{diamond} - 0.008$ v.e.

$$E = 10.745N_C + 3.703N_H + 2.545N_O - (K+\lambda) + E_N.$$

An error in the constants of this equation may affect the calculated bond energies E_{ij}, but will not affect the $\delta^{i}_{jj'}$, as is obvious from the previous discussion of additivity. (It may also be noted here that the introduction of the nuclear energies E_N alters what has been said of the additivity characteristics of $-(K+\lambda)$. Instead of these latter quantities the quantities $-(K+\lambda)+E_N$ will now have the same additivity characteristics as the energies E.)

Paraffins

In Table III are given the theoretical expressions for the electronic energies E of the

Table III.

Substance	E
CH_4	$4E_{CH}$
C_2H_6	$E_{CC}+6E_{CH}+6\delta^{C}{}_{CH}$
C_3H_8	$2E_{CC}+8E_{CH}+10\delta^{C}{}_{CH}$
C_4H_{10}	$3E_{CC}+10E_{CH}+14\delta^{C}{}_{CH}$
CH_3OH	$E_{OH}+E_{CO}+3E_{CH}+3\delta^{C}{}_{OH}+\delta^{O}{}_{CH}$
C_2H_5OH	$E_{OH}+E_{CO}+E_{CC}+5E_{CH}+2\delta^{C}{}_{OH}+\delta^{O}{}_{CH}+5\delta^{C}{}_{CH}$
$(CH_3)_2O$	$2E_{CO}+6E_{CH}+6\delta^{C}{}_{OH}$
$(C_2H_5)_2O$	$2E_{CO}+10E_{CH}+4\delta^{C}{}_{OH}+10\delta^{C}{}_{CH}$
H_2O	$2E_{OH}$
H_2O_2	$2E_{OH}+E_{OO}+2\delta^{O}{}_{OH}$
O_4	$4E_{OO}$ (?)

various compounds to be studied. The first energy difference in the normal paraffin series is $E_{CC}+2E_{CH}+6\delta^{C}{}_{CH}$, whereas all the other differences are of the same value $E_{CC}+2E_{CH}+4\delta^{C}{}_{CH}$. Rossini[3] has given accurate data for methane and ethane, but unfortunately there does not seem to be available any very accurate data on the higher members of the series. For the calculation of the nuclear energy of these two molecules assignments have been made for the fundamental modes of vibration by Vedder and Mecke[4] and by Eucken and Parts,[5] respectively. These data together with the heat of combustion of diamond should serve to determine fairly accurately the constants E_{CC}, E_{CH} and $\delta^{C}{}_{CH}$.

The nuclear energy is obtained as the sum of (1) the translational and rotational energy $(6/2)kT$, or $(5/2)kT$ for diatomic molecules, (2) the vibrational heat content as calculated from the Einstein equation, $\Sigma h\nu_0/(e^{h\nu_0/KT}-1)$, and (3) the zero-point energy $\Sigma h\nu_0/2$. In the case of diamond the zero-point energy was obtained by the application of Debye's equation for the specific heat of solids. The average frequency was calculated from the maximum frequency given by specific heat data. (This average frequency is very nearly the average of the observed Raman frequencies for diamond.) The heat content of diamond at 20°C, $\int_0^{293°K} C_v dT$, amounts to only about 0.01 v.e. per bond.

As will be seen in Table IV the nuclear energies

Table IV.

Substance	$E-E_N$	E_N	E (v.e.)
Diamond $C_n/2n$	3.330	0.130	3.460
CH_4	16.337	1.251	17.588
C_2H_6	27.565	1.971	28.536
CH_3OH	20.192	1.428	21.620
C_2H_5OH	31.673	2.212	33.885
$(CH_3)_2O$	31.172	2.120	33.292
$(C_2H_5)_2O$	53.914	3.393	57.307
H_2	4.440	0.320	4.760
H_2O	9.493	0.629	10.122
H_2O_2	10.99	0.706	11.696
O_3	6.15	0.258	6.408
O_4	10.19	0.316	10.51

are by no means very small quantities, but may amount to about one-tenth of the total energy in some cases. The calculated value of $\delta^{C}{}_{CH}$ is -0.05 v.e. (Table V). Hence the contribution per

Table V.

$E_{CC}=3.460$	$\delta^{C}{}_{CH}=-0.051$	$\Delta_{CH}=+0.287$
$E_{HH}=4.760$	$\delta^{O}{}_{CH}=-0.087$	$\Delta_{OH}=$?
$E_{OO}=$?	$\delta^{C}{}_{OH}=-0.266$	$\Delta_{CO}=$?
$E_{CH}=4.397$	$\delta^{C}{}_{CO}=-0.262$	
$E_{CO}=4.253$	$\delta^{O}{}_{OH}=$?	
$E_{OH}=5.061$	$\delta^{O}{}_{CO}=$?	

CH_2 group is about 0.2 v.e. As previously stated, Thomsen's values of the heat of combustion of the higher paraffins are probably not sufficiently accurate to make a fair test, since his value for ethane, for example, differs by about 0.2 v.e. from the more recent value of Rossini. Besides, it is at present not possible to make an accurate assignment of the fundamental modes of vibration in these molecules. If one does not take into consideration the correction for nuclear energy, Thomsen's data lead to successive energy differences which differ from one another by as much as 0.3 v.e. But the average of these differences, together with the constants obtained from methane and ethane, indicates that the nuclear energy per CH_2 group should be about 0.7 v.e. on the average. This is just about the value one would estimate from a consideration of the fundamental modes of vibration similar to that of Kohlrausch[6] in terms of group frequencies and

[4] H. Vedder and R. Mecke, Zeits. f. physik. Chemie **A86**, 137 (1933).

[5] Eucken and Parts, Zeits. f. physik. Chemie **B20**, 184 (1933).

[6] K. W. F. Kohlrausch, *Der Smekal-Raman Effect.*

valence frequencies. In fact, such a consideration shows that it would require an assignment of unreasonably high frequencies to account for the total discrepancies, i.e., on the assumption that $\delta^{C}_{CH}=0$.

Alcohols and ethers: Rossini has given accurate data on the heats of combustion of CH_3OH and C_2H_5OH, but for the nuclear energy it is necessary to make an estimate similar to that discussed above. Such an estimate will probably not be greatly in error, since the general range of the various frequency types is fairly well known from the Raman spectra. From these compounds and water one obtains E_{OH}, $(E_{CO}+\delta^{O}_{CH})$, and δ^{C}_{OH}.

For methyl and ethyl ether it was necessary to use Thomsen's data and to estimate the nuclear frequencies as before. Such a procedure may at least give an idea of the order of magnitude of the $\delta^{i}_{jj'}$ in question. From data on these and the previous compounds the values of E_{CO}, δ^{O}_{CH}, δ^{C}_{CO} were calculated.

The value -0.266 obtained for the constant δ^{C}_{OH} seems to indicate rather definitely that some of the $\delta^{i}_{jj'}$ may be considerably larger than $\delta^{C}_{CH}=-0.05$ v.e. It should be pointed out that the value for δ^{C}_{OH} was obtained from the accurate data of Rossini and an estimated value for the nuclear energy; and it seems very improbable that this estimated nuclear energy could be in error by an amount sufficient to account for the large value of δ^{C}_{OH}. On the other hand, the values for E_{CO}, δ^{C}_{CH} and δ^{C}_{CO} are much less certain than the previous values, since they are based partially on Thomsen's data for the ethers.

A list of the constants obtained for CHO compounds is given tentatively in Table V. It is of interest to note that the $\delta^{i}_{jj'}$ are all negative, whereas the Δ_{ij} are all positive.

Since values as great as 0.2 v.e. are rather definitely indicated by the accurate data on the alcohols, it therefore seems natural to ask the question whether in some cases the $\delta^{i}_{jj'}$ may not be even larger, and whether the peculiarities of some compounds, or the nonexistence of others, may not to some extent be connected with the existence of large interactions. For example, on the basis of thermochemical data alone, one might speculate concerning the nature of the bonds in O_3 and O_4 as follows.

In order to obtain the bond energy E_{OO} it would be convenient to have data on a compound containing only oxygen atoms and normal bonds, similar to the case of diamond for the bond energy E_{CC}. O_2 is, of course, excluded because of its magnetic properties, etc. O_3 and O_4 are ordinarily supposed not to contain normal bonds because of the large value of E_{OO} required as compared to that obtained from H_2O_2 on the assumption of perfect additivity. Nevertheless it may be of interest to see how large a value of δ^{O}_{OH} would be required to make these compounds fit into the present scheme. O_3 would not be suitable for the calculation of the normal bond energy E_{OO} because of the considerable strain implied by the triangular structure with normal bonds. On the other hand, O_4 would probably be only very slightly strained.

From O_4 the bond energy E_{OO} is thus calculated to be 2.63 v.e. (The nuclear energy is again estimated by comparison with that of ozone.) From H_2O_2 and H_2O one then obtains a value of -0.53 v.e. for δ^{O}_{HO}, which is only about twice that obtained for δ^{C}_{OH}, and of the same sign. Further, if one calculates the strain energy of O_3 relative to the bond energy in O_4, one obtains the value 1.48 v.e., which is of the same order of magnitude as that calculated by Pauling for trimethylene, 1.06 v.e. In Table VI are given the additional constants obtained from these questionable speculations:

TABLE VI.

$E_{OO}=2.63$	$\delta^{O}_{OH}=-0.53$	$\Delta_{OH}=+1.366$
		$\Delta_{CO}=+1.198$

The latter speculations are actually probably not valid, since the spectroscopic data of Ellis and others seem to indicate that O_4 consists of two loosely bound O_2 molecules. The latter calculations were made, however, simply to ascertain how large a value of the interaction increment δ^{O}_{HO} would be required for a normal O_4 structure. Since the value obtained was only twice that obtained in other cases, the argument sometimes given for abnormal bonds, on the basis of bond energies, seems questionable.

In view of the considerable limiting importance of the interactions $R^{i}_{jj'}$, as indicated by the $\delta^{i}_{jj'}$, it seems that Pauling's[7] resonance

[7] For a discussion of resonance energies see L. Pauling, reference 2, and L. Pauling and J. Sherman, J. Chem. Phys.

energies Δ_{ij} cannot be regarded as pure bond resonance energies. In fact, as was seen, the present considerations put only a sort of lower limit on the $R^{i}_{jj'}$, which may actually be considerably larger than is indicated by the $\delta^{i}_{jj'}$. Further, Pauling's bond energies were calculated without correcting for the nuclear energy, and therefore differ considerably from those obtained from the electronic energies. (The fact that Pauling's bond energies were calculated with reference to the excited state ^5S of the carbon atom has no effect on the resonance energies. It may be of interest to point out that Pauling estimated the excitation energy ^5S as 1.00 v.e.; whereas the extrapolation of recent spectral data of Edlén indicates a value of about 4.1 v.e. for this energy.) It also seems possible that the importance of the interaction energies, as well as of the nuclear energies, may be partially responsible for the fact that Pauling's electronegativity map cannot in all cases be correlated successfully with electric moment data.

Because of the scarcity of accurate data it does not at present seem worth while to extend the calculations to other types of compound. But mention should be made of the data of Kharasch[8] on several isomeric heptanes. The heats of combustion of all these isomers were found to be very nearly equal to one another; whereas the energies of formation would be expected to differ from one another in general. An accurate comparison should, however, take into consideration differences in heats of vaporization and in nuclear energies. It seems possible that the introduction of branched chains could alter these latter quantities considerably. Actually, data of Thomsen and others on the butanes and pentanes do indicate differences in the heats of combustion for the different isomers. The constancy in the observed heats of combustion for the isomeric heptanes might be due to a fortuituous compensation of the various factors involved.

In calculating the interaction constants $\delta^{i}_{jj'}$ it appears that these quantities may be quite considerable, but the corresponding deviations may often be compensated by nuclear energies, etc., and the departures from additivity thus masked in the ordinary previous types of analysis. It is therefore necessary that the data used should be very accurate in order to obtain reliable results. In order to make a further test of the present analysis it would be especially desirable to have combustion data on the higher alcohols, secondary and tertiary alcohols, glycols, cyclic paraffins, the esters of orthocarbonic acid, and the chlorine derivatives of methane and ethane. It is hoped that the present discussion will stimulate further research of this kind.

Double Bonds

The previous discussion was confined to molecules containing only single bonds; but in compounds where there is no appreciable resonance associated with the shift of a double bond, it is easily seen that the analysis can be extended to molecules containing double bonds, by considering a carbon atom with one or two double bonds as trivalent or bivalent, respectively, and using appropriate constants. For the case of two double bonds to a single carbon atom it would be of especial interest to have data on the compound allene.

1, 606 (1933). I am very much indebted to Dr. Sherman for helpful discussions and for kindly putting at my disposal a large amount of collected data on heats of combustion.

[8] M. S. Kharasch, Bur. Standards J. Research **2**, 359 (1929).

Analysis of Rotatory Dispersion Curves. II

Configurationally Related Substituted Fatty Acids

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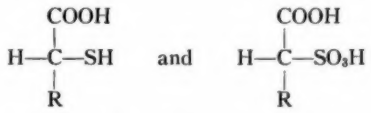
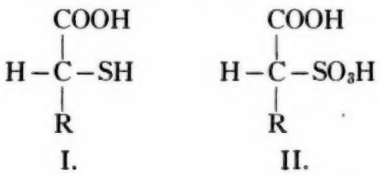
The rotatory dispersion curves of substituted fatty acids of the types



have been measured in the visible and ultraviolet regions. The results are in harmony with the rule previously reported that in members of homologous series, the total rotation of consecutive members may differ in sign, but the signs of the partial rotations remain constant.

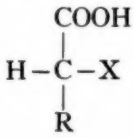
THE present communication deals with the analysis of the partial rotations of members of two configurationally related homologous series of substances of the following types:



I. II.

The members of the two series differ in the character of one substituent, namely, $-SH$ and $-SO_3H$, respectively. These two groups differ in their chromophoric properties and it was of interest to inquire, first, into the direction of the partial rotations of each of these groups, and second, into the partial rotations of the remaining parts of the molecules which are identical in the members of both series.

A further point of inquiry was the effect of ionization of the carboxyl group on the partial rotations. In carboxylic acids of the type



(where X=any functional group) ionization of the $-COOH$ group was found to produce a marked effect on the value of the rotation of the substance measured in the visible part of the spectrum and frequently to produce a change in the direction of the rotation. It was desired to ascertain whether the ionization of the carboxyl group has a similar rotational effect on the substances of the two series.

Levene, Mori and Mikeska[1] have reported observations on the rotations for the sodium D line of four members of the normal series of 2-mercapto acids and of the four corresponding sulfo acids and certain of their salts. They found that all the members of the series of the mercapto acids rotate in one direction, whereas the rotations of the higher members of the series of sulfo acids were in the opposite sense from those of the lower, the change of sign occurring between the second and third member. On the other hand, the rotations of the salts of the higher mercapto acids were in the opposite direction from those of the lower, but the salts of the sulfo acids all rotated in the same direction.

The following four acids were made the subject of the present investigation.

Dextro 2-mercaptobutyric acid (1) and its *Levo* monosodium salt.
Dextro 2-mercaptocaproic acid (1) and its *Dextro* monosodium and *Levo* disodium salts.
Dextro 2-sulfobutyric acid (1) and its *Levo* disodium and *Levo* calcium salts.
Levo 2-sulfocaproic acid (1) and its *Levo* disodium salt.

Inasmuch as interpretation of the dispersion curves depends on a knowledge of the absorption curves, the latter were made the subject of special study.

The results of the study of the absorption and dispersion curves may be summarized as follows:

[1] P. A. Levene, T. Mori and L. A. Mikeska, J. Biol. Chem. **75**, 337 (1927).

Absorption

Mercapto acids

The absorption curves of the two mercapto acids studied exhibit a definite maximum at 2400A. This band can safely be attributed to the SH group, inasmuch as 2-mercaptobutane has an absorption band in the same part of the spectrum, which is, however, slightly displaced towards higher frequencies (as is to be expected), and yet is still in a region of transparency for a simple aliphatic acid. The absorption curves of the sodium salts are less characteristic owing to the appearance of a strong second band (COO^-) which overlaps the SH band and masks its maximum (see Fig. 1).

Sulfo acids

The absorption curves of the sulfo acids present a characteristic maximum at 2150A (see Fig. 2). This band is doubtless the first COOH band displaced towards lower frequencies by the proximity of COOH to SO_3H, since we ascertained that an ordinary alkylsulfonic acid (2-methylpropylsulfonic acid(1)), has practically no absorption at all in that region and absorbs much less than the corresponding aliphatic acid.

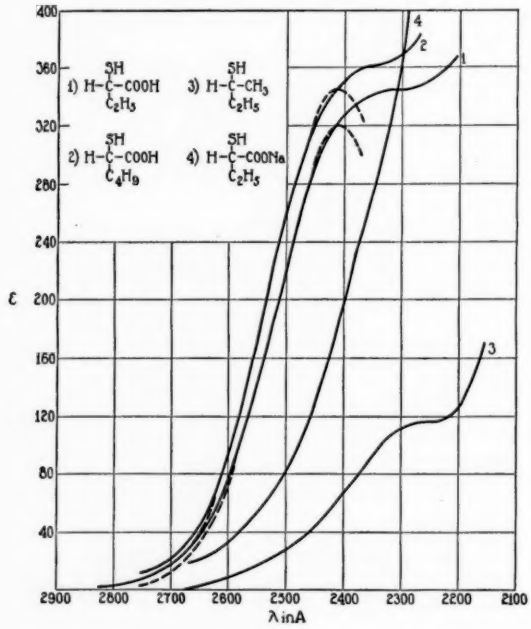


Fig. 1. Absorption curves of the mercapto acids and their sodium salts. The dotted curve is calculated.

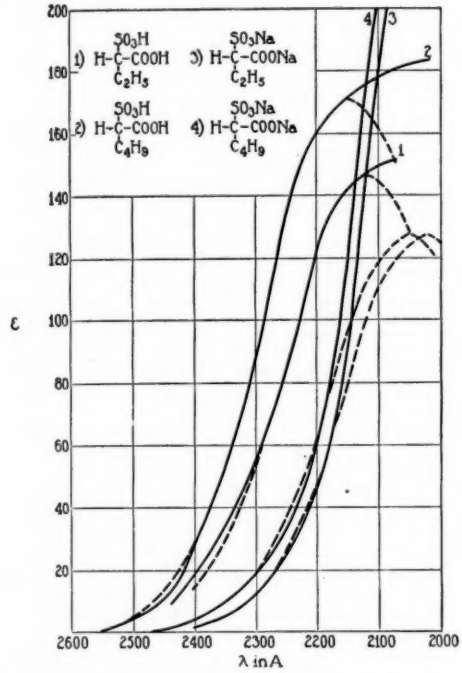


Fig. 2. Absorption curves of the sulfo acids and their sodium salts. The dotted curve is calculated.

The absorption curves of the sodium salts present a striking difference. The curve is displaced towards higher frequencies by about 150A, the maximum of the first band can no longer be seen and a continuous increasing absorption is observed as the wave-length becomes smaller. The fact that we have two bands overlapping each other and not one broad band is very well demonstrated by analysis of both absorption and dispersion curves. The striking change in the absorption is brought about by the ionization of the COOH group since the SO_3H group is already completely ionized in the free acid, as electrometric titration curves have shown.

Rotation

Mercapto acids

Analysis of the dispersion curves and direct dichroism measurements have shown that the first SH band is strongly coupled and that its rotatory contribution is predominant, i.e., the total molecular rotation has the sign of the SH partial rotation due to anisotropy of the $-SH$ band. The remainder of the rotation, the major

part of which can be attributed to the anisotropy of the COOH group, is of opposite sign.

The dispersion curves may be expressed by two dispersion terms (of Drude formula) of opposite sign, the dispersion constants λ_1 being practically the same for both compounds and the same being true for the λ_2 (see Tables III and V).

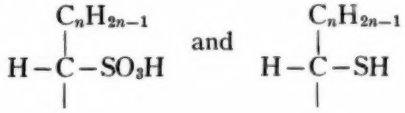
Sulfo acids

It was stated above that the rotations of the higher members of this series, beginning with the third, are of opposite sign from those of the lower.

The change in sign is due not to the change in sign of the partial rotations of the corresponding anisotropic groups, but to the fact that the absolute magnitude of the second partial contribution is greater than that of the first for the higher members, as a result of which their dispersion is anomalous. (Dispersion curve of case 4, see Levene, Rothen and Marker, reference 2, page 664.) The analysis of the dispersion curves of the free acids shows (see Tables VIII and XI) that the total rotation may be expressed by two terms of opposite sign, the first term having a constant of dispersion corresponding to the first absorption band of the carboxyl group (2120A for 2-sulfobutyric acid (1), 2150A for 2-sulfocaproic acid (1)). In the case of 2-sulfobutyric acid the second term is negative and the dispersion constant λ_2 is less than zero, indicating clearly an anomalous course of this term. In the case of 2-sulfocaproic acid the second term is likewise negative and the value of λ_2 approaches zero, thus indicating a similar anomaly.

These observations are in harmony with the rule, deduced from previously reported observations, to the effect that in *members of homologous series the total rotations of consecutive members may differ in sign but the signs of the partial rotations remain constant.*[2] Recently, Kuhn[3] made similar observations on the configurationally related inorganic complex salts.

If we consider the sulfo acids in relation to the mercapto acids, we see that the change $SH \rightarrow SO_3H$ produces a great rotatory effect which in small part may be due to the ionization of the group SO_3H. It may be mentioned, however, that the direction of the acid remains the same in an excess of mineral acid. The anisotropy of the carboxyl group is of opposite sign in the two series. In other words, the vicinal effect of the groups



and

induces opposite anisotropies in the carboxyl group.

Salts of mercapto acids

The opposite rotations observed in the visible region for 2-mercaptobutyric acid (1) and its salt are easily understood, since the dispersion curve of the salt has been found to be anomalous. No change of sign of anisotropy occurs on passing from the acid to the salt, but only a decrease in the magnitude of the partial rotation of the SH group which for the salt becomes smaller than the second contribution for $\lambda > 4046.6$A. Although the dispersion curves of the monosodium salts of these acids seem distinctly different, they can be expressed with precision by two dispersion terms having the same constants λ_1 and λ_2, respectively (see Tables IV and VI). The change of sign between 2-mercaptocaproic acid (1) and its disodium salt is easily explained in the same way (see Tables V and VII). In short, the anisotropy of the SH band increases from the lower to the higher members of the series and is greater for the free acid than for its salts.

Salts of the sulfo acids

The striking differences between the absorption of the sulfo acids and their salts are also found in their rotatory behavior. The dispersion curves of the salts can be resolved into two terms of opposite sign, each of them being of the opposite sign to the corresponding term for the free acid (see Tables IX, X and XII). The constant λ_1 of *the first term* is about 100A smaller than the corresponding λ_1 of the first term for the acid. It is very probable that the constants λ_1 of the acid and salt correspond to two different electronic states, despite the fact that they are of almost the same magnitude.

[2] P. A. Levene, Al. Rothen and R. E. Marker, Chem. Phys. **1**, 662 (1933).

[3] W. Kuhn and K. Bein, Zeits. f. anorg. Chem. **216**, 321 (1934).

Kuhn[4] arrived at analogous conclusions in a somewhat similar case when interpreting the dispersion curve of octyl nitrite. He assumed two different electronic states in the absorption band of NO_2 to explain two anisotropy factors of opposite sign in the same region of the spectrum.

The *second term* is strongly dispersive (λ_2 −1924A) in contrast to the anomalous second term of the acid.

Attention must be called to the fact that the dispersions of the thio and the sulfo acids were measured in different solvents. It is known that the direction of rotation of some substances changes with the change of solvent. However, this change was found to be due to the effect of the solvent on the numerical values of the individual partial rotations, the directions of the latter remaining unaltered.* In the special case of the thio-derivatives, the direction of rotation remains the same for both substances in ether or in water containing enough alcohol to effect the solution of the thio-derivatives.

Shape of Absorption Curves

The absorption curves of the mercapto acids, the sulfo acids and their salts were analyzed and it was found that they could be expressed by an exponential equation based on a Maxwellian distribution (as was first done by V. Henri,[5] and since then by Kuhn,[6] Lowry[7] and others.[7] In accord with the recent work of Lowry,[4] we found that better agreement between experimental and calculated rotation values was obtained by using a wave-length scale instead of a frequency scale. Consequently, our absorption curves have been expressed in the wave-length scale. We give below the parameters of the absorption curves for the different compounds, as calculated from the equation

$$\epsilon = \epsilon_{\max} e^{-[(\lambda-\lambda_0)/\theta]^2}$$

(where $\theta = \lambda'/1.665$, λ' is the **half**-width of the band and ϵ is the molecular extinction coefficient as defined in the *International Critical Tables*). Wave-lengths are expressed in microns to comply with the usual convention adopted in polarimetry. As may be seen from Figs. 1 and 2, only that part of the curve on the longer wave-length side of the origin λ_0 could be observed (see Table I).

Table I. *Absorption constants.*

Compound	Solvent	$\epsilon_{\max.}$	λ_0	θ
2-Mercaptobutyric acid (1)	heptane	320	0.2410	0.0159
2-Mercaptocaproic acid (1)	heptane	345	0.2410	0.0172
2-Sulfobutyric acid (1)	water	147	0.2120	0.0172
Na salt of 2-sulfobutyric acid (1)	water	128	0.2025	0.0180
2-Sulfocaproic acid (1)	water	172	0.2150	0.0180
Na salt of 2-sulfocaproic acid (1)	water	128	0.2050	0.0180

Table II. *Circular dichroism.*†

Compound	λ in A	$(\epsilon_l-\epsilon_r)\lambda$	$(\epsilon_l-\epsilon_r)_{\lambda 2410}$ Calc.	ϕ Calc. from dichroism data	ϕ Calc. from dispersion and absorption data
2-Mercaptobutyric acid (1)	2480	1.46±0.15	1.8$_5$	3700°	3600°
2-Mercaptocaproic acid (1)	2450	2.10±0.30	2.3	4600°	4680°
	2560	0.80±0.08			

It is interesting to note that in the case of the sodium salts of the two sulfo acids for which no maximum could be detected, the λ_0 which had to be chosen in order to represent correctly the first part of the absorption curve, had the same value as that found by dispersion measurements.

Rotatory Dispersion Formulae

According to Drude, the equation representing the rotation in the neighborhood of an active absorption band, has the form

$$[M] = \frac{A(\lambda^2-\lambda_0^2)}{(\lambda^2-\lambda_0^2)^2+\lambda'^2\lambda^2}.$$

The dispersion calculated from a simple term $A/(\lambda^2-\lambda_0^2)$ fixes the upper limit of the rotation. The rotation as we approach λ_ϕ (ϕ=maximum rotation) increases, although it never reaches the

* See W. Kuhn, *Stereochemie* of K. Freudenberg, p. 416, 1933 and Levene-Rothen-Meyer, Science **80**, 101 (1934).

[4] W. Kuhn and H. L. Lehmann, Zeits. f. physik. Chemie **B18**, 32 (1932).

[5] V. Henri and J. Bielecki, Phys. Zeits. **14**, 516 (1913).

[6] W. Kuhn and E. Braun, Zeits. f. physik. Chemie **B8**, 281 (1930).

[7] T. M. Lowry and H. Hudson, Phil. Trans. Roy. Soc. **A232**, 117 (1933). H. Hudson, M. L. Wolfrom and T. M. Lowry, J. Chem. Soc. 1933, 1179.

† See the relations between circular dichroism, anisotropy factor and maximum rotation of an active band, Hand- und Jahrbuch der chemischen Physik, *Drehung der Polarisationsebene des Lichtes*, von W. Kuhn und K. Freudenberg. Leipzig, 1932, p. 79.

value calculated from a simple term. On the other hand, the main characteristic of Kuhn's[6] recent dispersion formula (written with a λ scale as used by Lowry[7])

$$[M]=\frac{\phi}{m}\frac{\lambda_\phi}{\lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2}\int_0^{(\lambda-\lambda_0)/\theta}e^{x^2}dx+\frac{\theta}{2(\lambda+\lambda_0)}\right],$$

where m is the maximum value of the term inside the bracket, is that, for values of λ between $\lambda_{0+4\theta}$ and λ_ϕ the rotation increases more rapidly than if it were following a simple Drude term. Consequently, if a simple Drude term is used to express a dispersion over a wave-length interval which goes beyond the critical value $\lambda_{0+4\theta}$ then the value found for λ_0 is greater than the true value. We have found that, whenever sufficient precision was attained in the rotatory measurements in the neighborhood of the absorption band, Kuhn's equation was more satisfactory than Drude's. This is very well illustrated in

TABLE III. *Rotatory dispersion of dextro-2-mercaptobutyric acid (I) in heptane.*

Visible region: Concentration 1.1467M, $l=20$ cm. U.V. region: Concentration 1.1467 from 3990A to 3005A, 0.1147 from 2980 to 2770, $l=5$ cm from 3990A to 2843A, 1 cm from 2768A to 2370A. Measurements on levo form. The figures in the last column ($[M]^{25}$calc.) are calculated from the equation

$$[M]^{25}\text{calc.}=\frac{\phi}{0.556}\frac{\lambda_\phi}{\lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2}\int_0^{(\lambda-\lambda_0)/\theta}e^{x^2}dx+\frac{\theta}{2(\lambda+\lambda_0)}\right]-\frac{19.578}{\lambda^2-0.043}.$$

$\phi=3600°$, $\lambda_0=0.245$, $\theta=0.01537$, $\lambda_\phi=0.2560$.

This equation reduces for $\lambda>0.3065$ to

$$[M]^{25}\text{calc.}=\frac{25.4955}{\lambda^2-0.060}-\frac{19.5784}{\lambda^2-0.043}.$$

λ in A	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{19.1614}{\lambda^2-0.064}-\frac{13.2006}{\lambda^2-0.042}$	$[M]^{25}$calc.
5892.6	5.605	24.440	24.40	24.41
5780.1	5.9078	25.759	25.75	25.76
5460.7	6.947	30.293	30.29	30.31
4358.3	14.44	62.96	62.91	62.96
4046.6	19.19	83.678	83.67	83.59
3990	5.10	88.95	88.64	88.52
3815	6.10	106.4	107.5	107.1
3690	7.10	123.8	125.3	124.6
3593	8.10	141.3	142.8	141.6
3518	9.10	158.7	159.2	157.4
3445	10.10	176.1	178.3	175.8
3340	12.20	211.0	213.2	208.9
3260	14.10	245.9	247.9	241.8
3197	16.10	280.8	282.3	273.3
3145	18.10	315.7	317.0	
3098	20.10	350.6	354.6	339.1
3005	26.10	455.3	455.2	
2980	2.80	488	490.5	
2950	3.10	541	539.0	
2908	3.60	628	621.7	630.
2870	4.10	715	716.2	740.
2855	4.35	759	760	
2843	4.60	802	799	825
2770	1.27 conc. 0.0115M	1102	1125	1215
2620	0.30	2600		2660
2560	0.30	2600		2730
2483				430
2370	−0.29 conc. 0.057M	−5100		−4650

TABLE IV. *Rotatory dispersion of levo monosodium salt of 2-mercaptobutyric acid (I) in water containing 25 percent CH_3OH.*

Concentration: 0.7043M
Visible region: $l=20$ cm
U.V. region: $l=5$ cm from 3500 to 3110, 0.5 cm from 2950 to 2780.
Measurements on dextro form.

λ in A	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{5.150}{\lambda^2-0.062}-\frac{6.264}{\lambda^2-0.040}$
5780.1	−0.334	−2.37	−2.37
5460.7	−0.350	−2.485	−2.46
4358.3	−0.225	−1.60	−1.52
4046.6	0.00	0.00	0.00
3740	+0.15	+4.3	+3.45
3610	+0.25	+7.1	+6.0
3560	+0.35	+9.9	+7.3
3330	+0.65	+18.5	+16.9
3245	+0.85	+24.1	+23.1
3180	+1.05	+29.8	+29.2
3110	+1.25	+35.5	+37.9
2950	+0.25	+71	+72.6
2900	+0.35	+99	+91.0
2850	+0.45	+128	+116.0
2790	+0.55	+156	+159.6

TABLE V. *Rotatory dispersion of dextro-2-mercaptocaproic acid (I) in heptane.*

Visible region: concentration 0.6855M, $l=20$ cm.

U.V. region: concentration 0.6855M from 3965A to 2703A, 0.2285M for 2665A, 0.114M from 2585A to 2550A, 0.0571M from 2380A to 2340A, $l=5$ cm from 3965A to 2980A, 0.5 cm from 2920A to 2825A, 0.1 cm from 2785A to 2340A.

The figures in column 5 are calculated from

$$[M]^{25}\text{calc.}=\frac{\phi}{0.554}\frac{\lambda_\phi}{\lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2}\int_0^{(\lambda-\lambda_0)/\theta}e^{x^2}dx+\frac{\theta}{2(\lambda+\lambda_0)}\right]-\frac{20.140}{\lambda^2-0.045},$$

where $\phi=4680°$, $\lambda_0=0.245$, $\theta=0.0132$, $\lambda_\phi=0.255$.

This equation reduces for $\lambda>0.3000$ to

$$[M]^{25}\text{calc.}=\frac{28.415}{\lambda^2-0.060}-\frac{20.140}{\lambda^2-0.045}.$$

λ in A	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{20.249}{\lambda^2-0.064}-\frac{11.973}{\lambda^2-0.042}$	$[M]^{25}$calc.
5780.1	4.662	34.004	33.98	34.00
5460.7	5.447	39.73	39.73	39.75
4358.3	10.93	79.72	79.85	79.72
4046.6	14.34	104.59	104.3	104.3
3965	3.90	113.8	113.3	112.8
3750	4.90	143.0		
3590	5.90	172.1	174.3	172.4
3482	6.85	199.8		
3393	7.85	229.0	232.4	228.3
3322	8.85	258.2		
3215	10.85	316.6	319.3	310.2
3170	11.85	345.7	350.3	
3100	13.85	404.1		
3070	14.85	433.2	440.3	420.7
3042	15.85	462.4	472.0	449.1
3020	16.85	491.6	501.1	
2998	17.85	520.8		474.8
2980	18.85	550.0	560.7	526.8
2920	2.30	671	675.7	
2868	2.80	817	812.1	803
2825	3.30	948	964.4	965
2785	0.80	1170	1157	1173
2760	0.90	1310	1302	1330
2703	1.30	1900	1850	1940
2665	0.60	2620	2470	2500
2585	0.40	3510	6698	3650
2550	0.43	3800		3670
2380	−0.28	−4900		−5800
2340	−0.40	−7000		−6900

Tables III and V. The figures in columns 4 are calculated from a formula having two Drude terms, the constant λ_1 of the first term being 80A greater than the real value. Experimental and calculated rotations are in very good agreement over a considerable wave-length interval extending far beyond the critical value λ_{1+40} but, for values of λ approaching λ_ϕ, the calculated values have no longer any significance. For the near ultraviolet region, the figures found in columns 5 (which are calculated from a two term formula the first of which is a Kuhn term) do not check with the experimental values as well as do the figures in column 4, but are quite satisfactory for values of λ well within the band. Furthermore, the value of λ_1 of the Kuhn term is very near that found from absorption measurements for the head of this particular band. Part of the dispersion curve of the sodium salt of 2-sulfocaproic acid (1) may be seen in Fig. 3 (see Table XII). We have chosen this particular example since it illustrates very clearly how two different causes can produce an apparent shift of the value of λ_1 towards lower frequencies. The rotation from 5892.6A to 2822A of this salt, as well as that of the corresponding sulfobutyric acid, may be expressed within less than 0.5 percent by one Drude term. The value of the apparent λ_1 is 2186A, which is 136A higher than the value

TABLE VI. *Rotatory dispersion of dextro monosodium salt of 2-mercaptocaproic acid (1) in water containing 30 percent CH_3OH.*

Concentration: 0.3106M
Visible region: $l=20$ cm
U.V. region: $l=5$ cm

λ in A	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{5.767}{\lambda^2-0.062}-\frac{3.848}{\lambda^2-0.040}$
5780.1	+0.504	+8.11	+8.11
5460.7	+0.587	+9.45	+9.51
4358.3	+1.21	+19.5	+19.4
4046.6	+1.59	+25.6	+25.6
3700	+0.60	+38.6	+37.2
3450	+0.85	+54.7	+52.5
3330	+1.10	+70.8	+63.7

TABLE VII. *Rotatory dispersion of levo disodium salt of 2-mercaptocaproic acid (1) in water containing 20 percent CH_3OH.*

Concentration: 0.236M
Visible region: $l=20$ cm
U.V. region: $l=5$ cm

λ in A	α^{25}	$[M]^{25}$
5780.1	−0.244	−5.17
5460.7	−0.269	−5.70
4358.3	−0.255	−5.405
4046.6	−0.15	−3.18
3480	+0.35	+30
3350	+0.60	+51

TABLE VIII. *Rotatory dispersion of dextro 2-sulfobutyric acid (1) in water.*

Concentration: 0.8630M
Visible region: $l=40$ cm
U.V. region: $l=5$ cm from 3670A to 2835A, $l=1$ cm from 2620A to 2535A
Measurements on levo form.

λ in A	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{3.0656}{\lambda^2-0.045}-\frac{2.1733}{\lambda^2+0.030}$
5875.6	1.535	4.446	4.419
5780.1	1.600	4.635	4.635
5460.7	1.894	5.486	5.486
4358.3	3.89	11.27	11.27
4046.6	5.04	14.60	14.60
3670	0.90	20.8	21.0
3580	1.00	23.2	23.1
3500	1.10	25.5	25.3
3280	1.45	33.6	33.2
3160	1.70	39.4	39.1
3050	2.00	46.3	46.2
2975	2.25	52.1	52.1
2900	2.55	59.1	59.3
2835	2.80	64.9	67.0
2620	0.90	104	107.6
2585	1.00	116	118.0
2535	1.10	127	136.1

TABLE IX. *Rotatory dispersion of levo disodium salt of 2-sulfobutyric acid (1) in water.*

Concentration: 0.6517M
Visible region: $l=40$ cm
U.V. region: $l=5$ cm from 3450 to 2522A, 0.5 cm from 2500 to 2370A, 0.1 cm for (2335 and) 2320A.
Measurements on dextro form. The figures in the last column are calculated from the equation

$$[M]^{25}_{calc.}=-\frac{\phi}{0.562}\frac{\lambda\phi}{\lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2}\int_0^{(\lambda-\lambda_0)/\theta}e^{x^2}dx+\frac{\theta}{2(\lambda+\lambda_0)}\right]+\frac{28.640}{\lambda^2-0.037}.$$

$\phi=5140°$, $\lambda\phi=0.219$, $\lambda_0=0.2025$, $\theta=0.0180$.

for $\lambda>0.2750$ this equation reduces to

$$[M]^{25}=-\frac{36.039_5}{\lambda^2-0.041}+\frac{28.640}{\lambda^2-0.037}.$$

λ in A	α^{25}	$[M]^{25}$	$[M]^{25}=-\frac{7.4323}{\lambda^2-0.05385}$	$[M]^{25}_{calc.}$
5892.6	−6.605	−25.337	−25.333	−25.369
5780.1	−6.923$_5$	−26.560	−26.560	−26.560
5460.7	−7.947	−30.486	−30.417	−30.486
4358.3	−14.26	−54.70	−54.61	−54.70
4046.6	−17.63	−67.63	−67.63	−67.64
3780	−2.70	−82.9	−83.5	−83.2
3680	−2.95	−90.5	−91.1	−90.8
3585	−3.20	−98.2	−99.5	−98.8
3510	−3.45	−105.9	−107.2	−106.2
3445	−3.70	−113.5	−114.6	−113.2
3330	−4.20	−128.9	−130.3	−128.0
3235	−4.70	−144.2	−146.3	−142.9
3155	−5.20	−159.6	−162.7	−157.8
2840	−8.80	−270.1	−277.7	−253.0
2745	−10.80	−331.4	−345.7	−302.4
2680	−12.80	−392.8	−413.5	
2620	−15.60	−478.7		
2595	−16.80	−515.0		−492
2540	−19.80	−607.6		−598
2522	−20.70	−635.3		−644
2500	−2.30	−705.8		−706
2480	−2.55	−782.6		
2455	−2.80	−859		−862
2418	−3.30	−1013		−1038
2398	−3.80	−1166		
2370	−4.40	−1350		−1384
2320	−1.00	−1535		−1834

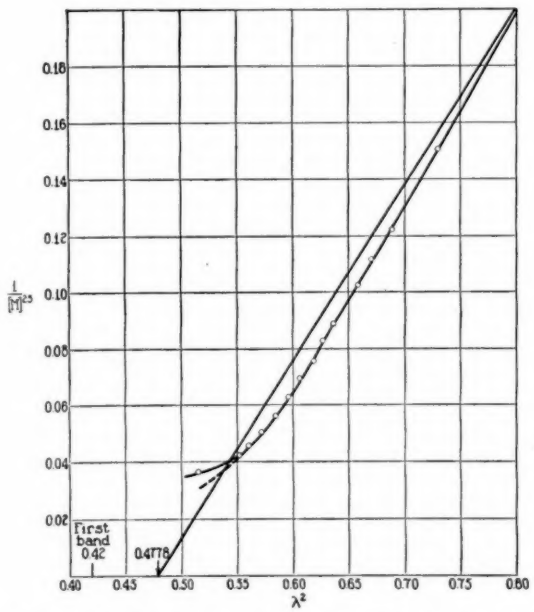


FIG. 3. Dispersion curve of the sodium salt of sulfocaproic acid. The dotted curve is calculated.

TABLE X. *Rotatory dispersion of levo calcium salt of 2-sulfobutyric acid (I) in water.*

Concentration: 0.33076M, visible region $l=40$ cm, U.V. region $l=10$ cm from 3980 to 2520A, 5 cm for 2340 and 2320A, 0.1 cm for 2270 and 2250A.

Measurements on dextro form.

The figures in the last column are calculated from the equation

$$[M]^{25}=-\frac{\phi}{0.562}\frac{\lambda_\phi}{\lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2}\int_0^{(\lambda-\lambda_0)/\theta}e^{x^2}dx+\frac{\theta}{2(\lambda+\lambda_0)}\right]+\frac{32.355}{\lambda^2-0.037}.$$

$\phi=5760°$, $\lambda_\phi=0.2190$, $\lambda_0=0.2025$, $\theta=0.0180$.

for $\lambda>0.2750$ this equation reduces to

$$[M]^{25}=-\frac{40.346}{\lambda^2-0.041}+\frac{32.355}{\lambda^2-0.037}.$$

λ in A	α^{25}	$[M]^{25}$	$[M]^{25}=-\frac{8.0476}{\lambda^2-0.0542}$	$[M]^{25}$calc.
5780.1	−3.804	−28.75	−28.75	−28.75
5460.7	−4.367	−33.01	−32.98	−33.36
4358.3	−7.85	−59.3$_3$	−59.29	−59.33
4046.6	−9.72	−73.4$_7$	−73.47	−73.42
3980	−2.55	−77.1	−77.2	−77.2
3670	−3.30	−99.8	−100.0	−99.4
3540	−3.80	−114.9	−113.2	−112.1
3410	−4.30	−130.0	−129.7	−127.8
3300	−4.80	−145.1	−147.1	−138.4
3220	−5.30	−160.2	−162.7	−158.4
3155	−5.80	−175.3	−177.5	−171.9
3045	−6.80	−205.6	−209.0	−199.4
2965	−7.80	−235.8	−238.8	−224.6
2896	−8.80	−266.0	−271.3	−250.8
2830	−9.80	−296.3	−311.0	−281.2
2753	−11.80	−356.7	−372.9	
2688	−13.80	−417.2	−446.1	
2600	−17.80	−538.1		−534
2565	−19.80	−598.6		−611
2540	−21.80	−659.1		−670
2520	−23.80	−719.5		−723
2340	−2.80	−1690		−1800
2320	−3.30	−1995		−2200
2270	−0.70	−2120		−2600
2250	−0.80	−2420		−2775

TABLE XI. *Rotatory dispersion of levo 2-sulfocaproic acid (I) in water.*

Concentration: 0.6830M, visible region $l=40$ cm, U.V. region $l=10$ cm for 3560 and 3270A, 5 cm, for 3450A, 1 cm for 2700A, 0.1 cm for 2400A.

λ in A	α^{25}	$[M]^{25}$	$[M]^{25}=\frac{3.0626}{\lambda^2-0.0462}-\frac{6.5309}{\lambda^2-0.007}$
5892.6	−2.465	−9.023	−9.022
5780.1	−2.548	−9.326	−9.328
5460.7	−2.809	−10.282	−10.275
4358.3	−3.93	−14.38	−14.39
4046.6	−4.26	−15.59	−15.61
3560	−1.10	−16.1	−16.5
3450	−0.53	−15.5	−16.2
3270	−1.00	−14.6	−14.9
2700	+0.20	+2.9	+15.6
2400	+0.22	+32	+102.2

TABLE XII. *Rotatory dispersion of levo disodium salt of 2-sulfocaproic acid (I) in water.*

Concentration: 0.2572M, visible region $l=40$ cm, U.V. region $l=10$ cm from 3790 to 2520A, 1 cm from 2520 to 2350A, 0.1 cm for 2270.

The figures in the last column are calculated from the relation

$$[M]^{25}=-\frac{\phi}{0.562}\frac{\lambda_\phi}{\lambda}\left[e^{-[(\lambda-\lambda_0)/\theta]^2}\int_0^{(\lambda-\lambda_0)/\theta}e^{x^2}dx+\frac{\theta}{2(\lambda+\lambda_0)}\right]+\frac{21.271}{\lambda^2-0.037}.$$

$\phi=5290°$, $\lambda_\phi=0.2210$, $\lambda_0=0.2050$, $\theta=0.0180$.

for $\lambda>0.2770$ this expression reduces to

$$[M]^{25}=-\frac{37.437}{\lambda^2-0.042}+\frac{21.271}{\lambda^2-0.037}.$$

λ in A	α^{25}	$[M]^{25}$	$[M]^{25}=-\frac{16.197}{\lambda^2-0.04778}$	$[M]^{25}$calc.
5892.6	−5.560	−54.04	−54.09	−54.09
5780.1	−5.820	−56.57	−56.57	−56.57
5460.7	−6.649	−64.63	−64.68	−64.69
4358.3	−11.725	−113.97	−113.93	−113.97
4046.6	−14.37	−139.7	−139.7	−139.7
3790	−4.35	−169.1	−169.0.	−168.8
3720	−4.60	−178.8	−178.8	−178.6
3600	−5.10	−198.3	−198.0	−197.7
3490	−5.60	−217.7	−218.8	−218.3
3410	−6.10	−237.2	−236.4	−235.6
3327	−6.60	−256.6	−257.5	−256.4
3265	−7.10	−276.0	−275.4	−273.9
3150	−8.10	−314.9	−314.8	−312.5
3055	−9.10	−353.8	−355.6	−352.7
2980	−10.10	−392.7	−394.8	−389.2
2920	−11.10	−431.6	−432.1	−424.6
2868	−12.10	−470.4	−469.8	−460.0
2822	−13.10	−509.3	−508.4	−495.8
2761	−15.10	−587.1	−569.3	
2702	−17.10	−664.8	−642.0	
2625	−21.10	−820.4	−766.7	−805
2590	−23.10	−898.1		
2567	−25.10	−975.9		−940
2541	−27.10	−1053.6		
2520	−29.10	−1131.4		
2520	−2.90	−1128		−1110
2504	−3.10	−1205		
2487	−3.40	−1322		
2460	−3.70	−1438		−1395
2445	−4.10	−1594		
2415	−4.60	−1788		1720
2390	−5.10	−1983		1954
2365	−5.60	−2177		
2350	−6.10	−2372		2390
2270	−0.70	−2720		3330

found from absorption measurements. This shift is due to our having neglected a second term of opposite sign. Now, for values of λ smaller than the critical value $\lambda_{0+\theta}$ the dispersion becomes still greater and λ_1 seems shifted still further towards lower frequencies. This second shift is produced because the rotation increases accord-

ing to a Kuhn term and not a Drude term. In fact, the dispersion curve may be fairly well represented by two terms of opposite sign, the first one being a Kuhn term with a value λ_1 equal to that found from absorption measurements.

Circular Dichroism

In the case of the mercapto acids, measurements of circular dichroism were made by the method used by Kuhn.[8] Because of experimental difficulties, our results are not very accurate. However, the order of magnitude of the circular dichroism found for the SH band is quite in accord with the maximum partial rotation contributed by that band as calculated from the dispersion curves. Our results are summarized in Table II.

Experimental

Compounds

The compounds were obtained by the methods previously described by Levene, Mori and Mikeska,[1] with the exception of 2-sulfobutyric acid (1) which was prepared and resolved according to Backer.**

All the compounds were carefully analyzed. Titrations indicated that the mercapto acids were at least 99.8 percent pure. The analyses of the sulfo acids were performed on their Ba salts.***

Apparatus

The instruments described in a previous article[2] were used to determine the rotatory dispersions in the visible and the ultraviolet regions. The same general procedure was followed and the same precision is claimed. Absorption measurements were carried out with a Hilger sector photometer in conjunction with a Hilger quartz spectrograph model E316.

Unless otherwise indicated, wave-lengths are expressed in microns in all formulae employed.

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[8] W. Kuhn and E. Braun, Zeits. f. physik. Chemie **B8**, 445 (1930).

** The values of the molecular rotations given are not to be taken as maximum rotations since no attempt was made to resolve the compounds to the maximum, hence no special precaution was taken to determine precisely the *absolute* rotations, as the main purpose of this work was to obtain accurate dispersion measurements. However, the *ratio* of the rotations of the acids to those of their respective salts must be considered as characteristic of the compounds, since the same source of material was used to determine the dispersion of the acids and their salts. Backer and Boer [H. J. Backer, J. H. de Boer, Rec. trav. chim. **43**, 297 (1924)] had previously resolved 2-sulfobutyric acid (1). The value they obtained for the maximum rotation of the calcium salt was $[M]_{5892} = -25.3°$, as compared to our own value $[M]^{25}_{5892} = -27.46°$. (Their value has been recalculated from their own function $[M] = f(c)$ for the concentration at which we made our measurements.) The dispersion data given by these authors for a short wave-length interval are in accord with our own measurements. We determined accurately the following ratio

$$\frac{[M]^{25}_{57801}\ \text{Ba salt}}{[M]^{25}_{57801}\ \text{acid}} = -6.28°,$$

which is not in accord with the value $-3.27°$ recorded by Backer. Furthermore, the dispersion of this acid as given by Backer is completely different from our own curve. These discrepancies induced us to repeat our measurements but we found that our results were readily duplicated.

*** We are indebted to Dr. G. M. Meyer of this department for the preparation of a sample of 2-mercaptobutyric acid (1).

Pressure Coefficients of Acoustic Velocity for Nine Organic Liquids

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With a pressure supersonic interferometer especially devised for this purpose, nine organic liquids are examined at frequencies a little less than 200 kc and at temperatures varying from 22.7°C to 25.5°C for the various liquids. The acoustic velocity is measured at intervals from atmospheric pressure to a pressure of 300 kg/cm². The values of the acoustic velocity (in meters per second) in the liquids at the pressures indicated are given below:

Liquid	C_2H_5Br	$C Cl_4$	$CHCl_3$	$C_2H_5OC_2H_5$	C_5H_{12}	CS_2	C_6H_6	C_7H_8	$C_6H_5NH_2$
Atmospheric Pressure	885.	912.	986.	993.	1005.	1136.	1290.	1313.	1640.
300 kg/cm² Pressure	1000.	1048.	1097.	1255.	1281.	1268.	1416.	1447.	1745.

This method is being used for the determination of the value of the specific heats at other than atmospheric pressure.

TEMPERATURE and pressure coefficients of acoustic velocity in liquids serve a useful purpose in the evaluation of thermodynamic coefficients. Temperature coefficients of acoustic velocity at atmospheric pressure are already available for a number of liquids but thus far no attempt appears to have been made to measure the effect of change of pressure on the acoustic velocity in liquids.

An instrument has been devised for this purpose[1] following closely the design of the sonic interferometer for liquids of Hubbard and Loomis,[2] modifications being made so as to permit measurements at different pressures. The instrument consists essentially of a cylindrical liquid chamber, about 6.1 cm in diameter (crystal and reflector slightly smaller) and approximately the same in length, of about 250 cc capacity, in a block of special cast steel of dimensions $8\times5\times5$ inches. Within the chamber is placed the acoustic system which consists essentially of a piezo-electric quartz disk, a moving reflector parallel to the surface of the disk and the liquid to be studied. The quartz disk is sputtered with gold on its two faces and rests upon a disk of Bakelite in the bottom of the chamber. Four external outlets from this chamber are provided: one for the lead wire to the lower electrode surface of the quartz, the upper electrode being grounded to the body of the instrument; a second outlet permits the screwing of a piston in it to serve as a means of adjusting the pressure in the liquid; through the third outlet passes the shank of a shaft accurately threaded on the part inside the chamber, so as to control and measure the to-and-fro movement of the reflector without disturbing the pressure in the liquid; and a fourth outlet provides connection to a Bourdon gauge of $\frac{1}{2}$ of one percent accuracy. The quartz disk in the interferometer chamber, when excited at a frequency in the neighborhood of 200 kc, is set into vibration and constitutes the source of the acoustical waves. The maximum wave-length in the liquids used was of the order of 0.8 cm while the diameter of the liquid chamber was of the order of 6.1 cm. Thus the ratio of the diameter of the liquid chamber to the wave-length is of such magnitude that no tube corrections are necessary.

Resonance positions of the reflector, one-half acoustic wave-length apart, were determined by the electro-acoustic method of Hubbard and Loomis.[2] A Hartley oscillator was used to drive the crystal and its frequency was measured by a General Radio precision wave meter calibrated at the Bureau of Standards, two other such wave-meters being used as a check upon its constancy of calibration. The experiments were carried out in a room below ground level so that special temperature regulation was not considered necessary, the temperature changing only a fraction of a degree during a run upon a given

[1] J. Chester Swanson, R. S. I. **4**, 603–605 (1933).
[2] J. C. Hubbard and A. L. Loomis, Phil. Mag. **5**, 1178 (1928).

TABLE I. *Measured values of the acoustic velocity.*

Liquid	Pressure kg/cm²	Velocity m/sec.
C_2H_5Br	Atmos.	886.
	179.	948.
(24.7°C)	153.	941.
	197.	962.
(197.7 kc)	216.	971.
CCl_4	Atmos.	912.
	35.	928.
	49.	936.
(23.0°C)	77.	959.
	118.	966.
(197.8 kc)	162.	986.
	216.	998.
$CHCl_3$	Atmos.	986.
	38.	1001.
(22.7°C)	49.	1007.
	72.	1019.
(196.5 kc)	98.	1024.
	120.	1029.
	141.	1036.
	170.	1050.
	181.	1053.
	211.	1062.
$C_2H_5OC_2H_5$	Atmos.	994.
	30.	1025.
(23.6°C)	42.	1029.
	63.	1050.
(196.6 kc)	77.	1061.
	79.	1063.
	96.	1076.
C_5H_{12}	Atmos.	1006.
	43.	1051.
(23.9°C)	70.	1071.
	98.	1093.
(197.7 kc)	113.	1104.
	114.	1108.
CS_2	Atmos.	1137.
	25.	1154.
(23.5°C)	34.	1151.
	63.	1171.
(193.9 kc)	88.	1174.
	111.	1178.
	118.	1189.
	152.	1185.
	178.	1215.
	218.	1214.
C_6H_6	Atmos.	1285.
	35.	1306.
(25.5°C)	74.	1325.
	94.	1337.
(193.7 kc)	155.	1363.
	184.	1377.
	210.	1383.
	229.	1388.
	250.	1394.
	281.	1403.
	301.	1410.
	350.	1438.
C_7H_8	Atmos.	1311.
	35.	1330.
(25.0°C)	56.	1346.
	71.	1353.
(172.0 kc)	83.	1353.
	130.	1368.
	155.	1385.
	177.	1392.
	194.	1399.
	270.	1434.
	310.	1460.
$C_6H_5NH_2$	Atmos.	1647.
	60.	1659.
(23.7°C)	99.	1677.
	136.	1687.
(197.7 kc)	183.	1707.
	288.	1737.

liquid; the mean temperature of all the measurements was 24°C and the maximum departure from the mean for any one liquid was 1.5°C. Time was allowed for temperature equilibrium to be reached after the adiabatic heating or cooling of the liquid caused by adjustments of pressure. Equilibrium was hastened by the reflector being moved up and down for that purpose. Moreover, the large mass of metal in the instrument (100 lbs.) reduced net departures of equilibrium temperature within the instrument from the temperature of the room to a fraction of a degree.

The liquids used were Baker's analyzed C.P. chemicals and were chosen so as to provide a wide range of densities, compressibilities, viscosities and sound velocities.

Table I gives the experimental data consisting of the temperature and frequency for each liquid, and the run of pressures and corresponding velocities in meters per second for each liquid. Fig. 1 shows the relationship between velocity and pressure. In the relatively small pressure range of these experiments a nearly linear relationship between pressure and velocity is to be expected and such a relationship is found to represent best the experimental results, in most cases within the errors of measurement. It should be noted that the velocities at atmospheric pressure are in exceedingly good agreement with those before obtained.[3] As the pressure increases, pentane and ether show approximately twice the

[3] E. B. Freyer with J. C. Hubbard and D. H. Andrews, J. Am. Chem. Soc. **51**, 759 (1929).

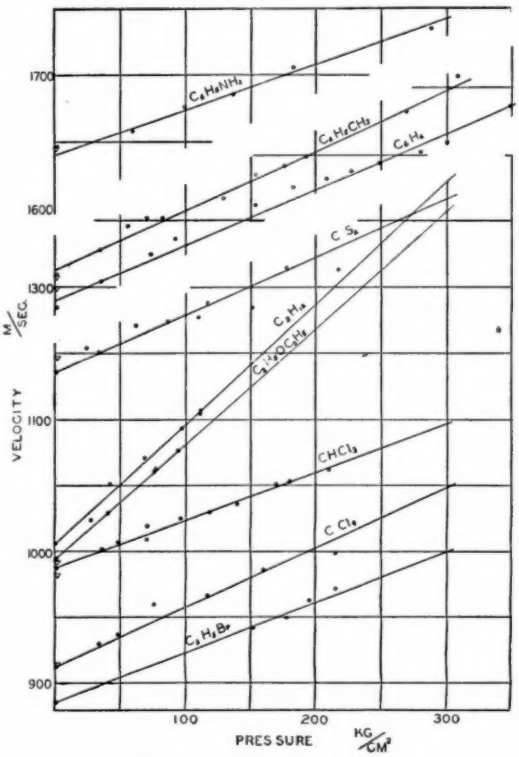

FIG. 1. Experimentally determined values of the acoustic velocity in liquids under pressure. The triangular marks at atmospheric pressure show the values obtained by Freyer[3] of the acoustic velocity for these liquids.

variation of velocity with pressure shown by the remaining seven liquids in the same pressure range. Table II gives the value of the velocity at atmospheric pressure and a pressure of 300 kg/sq. cm and summarizes the average change of velocity within this range in pressure units of 100 kg/sq. cm and 1000 lbs./sq. in.

Apparently no previous attempt has been made to study the effect of pressure on the acoustic velocity of liquids. The only means at hand therefore of checking the present results is by the use of thermodynamic relationships. By this method, however, it is possible to obtain pressure-velocity curves for only three of the liquids studied because of the scarcity of values of isothermal compressibility, dilatation and specific heats at other than atmospheric pressure. Bridgman's[4] results were obtained for regions of pressure much higher than those here studied, although his work is supplemented in some cases by that of Amagat and an extrapolation of his own values in this pressure range. It was found impossible to measure the acoustic velocity in several of the liquids studied by Bridgman without extensive alterations in the interferometer, owing to the fact that in the present design the liquid comes into direct contact with the piezoelectric disk and in many samples of liquid available there was sufficient conduction to prevent the production of acoustic waves.

The three liquids for which thermodynamic computations of velocity are possible are carbon disulphide, ether and ethyl bromide. The thermodynamic quantities needed for the computation of acoustic velocity (μ) in liquids are density (ρ), isothermal compressibility (β_τ) and ratio of specific heats (k); or density and adiabatic compressibility (β_ϕ). When the isothermal compressibility is used, the relationship is:

$$\mu = (k/\rho\beta_\tau)^{\frac{1}{2}}.$$

This method has the disadvantage of making the specific heats a most significant factor and of all the thermodynamic quantities used they are acknowledged to be the least accurate. For the liquids studied the ratio of specific heats in this pressure range was available in only one case For these reasons no results from the use of this method are given although we have attempted to use it. When the adiabatic compressibility is used, the relationship is given by the equation:

$$\mu = (1/\rho\beta_\phi)^{\frac{1}{2}}.$$

TABLE II. *Pressure coefficients of acoustic velocity.**

Liquid	Velocity in meters per sec. Pressure 1 atmos.	Velocity in meters per sec. Pressure 300 kg/cm²	Average change in velocity m/sec. 100 kg/cm²	Average change in velocity m/sec. 1000 lb./in.²
Ethyl bromide	885.	1000.	38.3	26.9
Carbon tetrachloride	912.	1048.	45.3	31.8
Chloroform	986.	1097.	53.0	23.2
Ethyl ether	993.	1255.	87.3	61.4
Pentane	1005.	1281.	92.0	64.7
Carbon disulphide	1136.	1268.	44.0	30.9
Benzene	1290.	1416.	42.0	29.5
Toluene	1313.	1447.	44.7	31.4
Aniline	1640.	1745.	35.0	24.6

* The values at both atmospheric pressure and 300 kg/cm² are taken from a straight line drawn through the average positions of the experimentally determined values. (Fig. 1.)

[4] P. W. Bridgman, Proc. Am. Acad. Arts and Sci. **49**, 4–114 (1913).

The disadvantage of this method is that the adiabatic compressibility does not lend itself to ready measurement and therefore, instead of from an experimentally determined value, it must be obtained from the relationship:

$$\beta_\phi = (1/v)(\partial v/\partial P)_\phi$$
$$= (1/v)[(\partial v/\partial P)_T + (T/C_p)(\partial v/\partial T)^2_P].$$

Where $(\partial v/\partial P)_T$ is the isothermal differential coefficient of compressibility, $(\partial v/\partial T)_P$ is the differential coefficient of dilatation at constant pressure, T is the absolute temperature and C_p is the specific heat at constant pressure. These quantities are available for several of the liquids studied. The specific heat at constant pressure also enters in this determination but here it is the divisor of the square of a very small quantity, the whole term merely acting as a correction factor for the isothermal compressibility. This becomes of importance in the computations since the variation of C_p with pressure could be obtained for only one of the liquids. In the case of carbon disulphide Bridgman gives the change of C_p with pressure in this pressure range. The variation between atmospheric pressure and a pressure of 300 kg/cm² was 1.7 percent and for the other liquids for which Bridgman gives values of C_p in this pressure range, the variation is about this value. Such a change of C_p in the above equation would be negligible and so we feel justified in giving these computed values even though we must use a constant value of C_p.

The results of applying these methods to the only three liquids for which data were available is shown in Fig. 2. The solid lines show the experimental values while the dashed curves show the computed values. The quantities used in the computations are those taken from the work of Bridgman except when otherwise noted. It should be pointed out, however, that had computations been made from some of the data from more recent sources better agreement between calculated and experimental values are attained than with the extrapolations given by Bridgman. We have preferred in this initial study to take all of our thermodynamic data from a single source, namely, that of Bridgman. The value of the specific heat at constant pressure at atmospheric pressure in every case was taken from the *International Critical Tables*. Bridgman gives

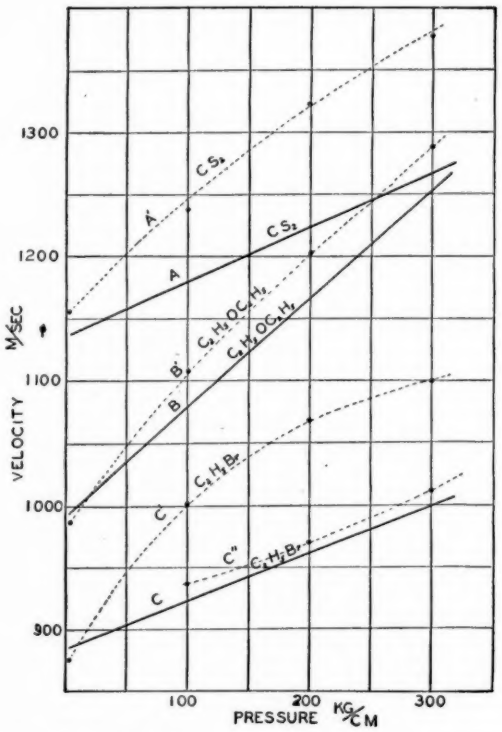

FIG. 2. The relationship between computed and experimentally determined values of the acoustic velocity in liquids under pressure. The solid lines show the experimental values, the dashed lines the computed values.

only the change of specific heats with pressure. The correlation between the calculated and experimental values is not as good as we had expected. However, considering the uncertainty of the values of many of the thermodynamic coefficients used in the computations, they are in very good agreement. In some instances the values given by different observers varied as much as twenty percent.

CARBON DISULPHIDE

For carbon disulphide the computed values increase with increase of pressure more rapidly than the experimental values and have a higher value at atmospheric pressure. It is unfortunate that while the results available for carbon disulphide are the most complete they are less accurate than those for many other liquids. At the same time the experimental values for carbon disulphide are not as reliable as those for the other liquids. Often upon removing the liquid from the instrument, some corrosive action was

noted. This lack of purity of the liquid we feel sure explains the discrepancy between these measurements at atmospheric pressure and those of Freyer[3] (shown in Fig. 1). Freyer used a gold plated liquid chamber and the highest degree of purity. This state of purity could not be maintained in this instrument and was not considered necessary in this initial study. The experimental determination was at a temperature of 23.5°C and the computed values are also for this temperature.

Ethyl Ether

Bridgman states that the thermodynamic properties within this pressure range "are rather more than usually accurate for ether." The computed and the experimental values for ether are in much better agreement than for any other liquid. The experimental values were taken at a temperature of 23.6°C. The data were not available to compute values at this temperature, so the calculated values are for a temperature of 20°C. Since an increase of temperature causes a decrease of velocity in ether, these curves would be in better agreement if it had been possible to obtain the values at the same temperature.

Ethyl Bromide

Richards[5] has done some later work on compressibilities in this pressure range and his values of the isothermal compressibility for ethyl bromide vary by almost twenty percent from those given by Bridgman. So we give two computed curves for this liquid. Curve C' is computed as was the curve for the other liquids, from the values of Bridgman. Curve C'' uses the same data as curve C' except for the values of the isothermal compressibility, which in this case are taken from Richards. Richards gives his values as average compressibilities over rather wide pressure ranges, but by a graphical method it is possible from his results to compute the values at pressures of 100, 200, 300 and 400 kg/cm². He gave no values for atmospheric pressure so we do not draw the curve below a pressure of 100 kg/cm². Here again it was impossible to obtain the calculated values at exactly the same temperature as the experimental determination. The calculated curves are for 20°C and the experimental values were taken at a temperature of 24.7°C. A better agreement between observed and calculated values than that shown here is accordingly to be expected when sufficient data are at hand to make a comparison possible at the same temperatures.

It is the purpose of the author to make a more comprehensive study of these and other liquids, in particular at precisely controlled temperatures, using the method described as a basis for the determination of the ratio of specific heats and other thermodynamic coefficients at other than atmospheric pressure.

It is with a great deal of pleasure that I acknowledge the constant assistance and encouragement of Professor J. C. Hubbard of the Johns Hopkins University. The measurements were taken in his laboratory at the Johns Hopkins University.

[5] T. W. Richards, J. Am. Chem. Soc. **34**, 988 (1912); **38**, 998 (1916).

The Entropy of Polyatomic Molecules

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A general expression for the entropy of the polyatomic molecule, rigid in the sense that only one form with a given set of moments of inertia is possible, is tested by comparison of calculated and experimental values. The results are satisfactory for molecules with as many as seven rotational degrees of freedom.

THE entropy of the polyatomic molecule is expressed as the sum of three separable contributions, arising, respectively, from translation, rotation and internal vibration. The translational entropy, per mole, is expressed by the equation,

$$S_{\text{tr}} = R \ln \frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} e^{5/2}, \qquad (1)$$

in which R is the gas constant, V the molal volume, N is Avogadro's number, m is the mass of the molecule, k the Boltzmann constant, T is the absolute temperature, h is Planck's constant and e is the natural logarithmic base. At low pressures, such that the ideal gas laws are approximately obeyed, this expression is highly accurate regardless of the complexity of the molecule.

It is the rotational contribution which presents the principal problem in the complex polyatomic molecule. Expressions have been derived from fundamental mechanical principles for rigid molecules with two and three rotational degrees of freedom, and for the type represented by ethane in which two entirely equivalent parts rotate independently about a common axis. This latter derivation, by Mayer, Brunauer and Mayer,[1] presents rather formidable mathematical difficulties, from which it would appear that the similar derivation for the molecule with n independently rotating parts oriented at various angles to one another, would be extremely difficult if not impossible. However, an examination of the several equations which have been quoted or derived in the above paper shows them to be of the following form:

$$S_{\text{rot}} = R \ln \frac{1}{\pi\sigma}\left\{\frac{8\pi^3(A^aB^bC^c\cdots G^g)^{1/n}kTe}{h^2}\right\}^{n/2}. \qquad (2)$$

[1] Mayer, Brunauer and Mayer, J. Am. Chem. Soc. **55**, 37 (1933).

Here A, B, etc., are the moments of inertia of the molecule and its independently rotating parts; a, b, etc., are the rotational degrees of freedom associated with the corresponding moments of inertia; $a+b+c+\cdots+g=n$ is total number of rotational degrees of freedom, and σ is the symmetry number, defined as the number of indistinguishable permutations produced by rotation of the molecule or its parts. It is not unreasonable to suppose that this equation may apply in the generalized form to molecules of different symmetry, and with more rotational degrees of freedom than those for which it was originally derived. It is the purpose of this paper to show that for such substances a satisfactory agreement with experimental entropies is obtained. The comparisons with experimental data have been restricted to cases in which the molecules are rigid in the sense that no "optically isomeric" forms are possible, such as the alternative forms of *n*-butane.

The vibrational entropy is expressed by the equation:

$$S_{\text{vib}} = R\sum_{i=1}^{i=3N-3-n} \frac{h\nu/kT}{e^{h\nu/kT}-1} - \ln\,(1-e^{-h\nu/kT}), \quad (3)$$

a summation over i frequencies of numerical value ν. This function is at best only approximate, and its application is somewhat restricted by the arbitrary nature of the selection of fundamental frequencies and their degeneracy. Molecules of low molecular weight have almost negligible total vibrational entropy, while the typical complex organic molecule has a sufficient number of low fundamental frequencies to make the vibrational entropy a contribution of considerable magnitude. In other words, the magnitude increases rapidly with the molecular weight, and, with our present knowledge of molecular vibrations, the uncertainty of the estimate increases still more

rapidly. As a result, the examples selected for the present purpose, primarily a test of Eq. (2), must be such as to introduce through the vibrational terms a maximum error which is small by comparison with the contribution due to a single rotational degree of freedom.

The procedure by which the vibrational entropy of acetone has been estimated may be taken as an example. The frequencies are taken from the Raman spectrum by Dadieu and Kohlrausch.[2] The decision as to the single or multiple character of the frequencies requires an attempt to describe the motions. For this purpose, the approach described by Dennison[3] and the considerations of three particle systems by Cross and Van Vleck[4] are very helpful.

The contribution of the lower frequencies is most important according to Eq. (3), those above 1000 cm^{-1} contributing little to the entropy. The acetone frequencies, with the approximate description of the probable motions represented by them, the corresponding multiplicity (m), and the entropy contribution (S), are summarized in Table I. The accuracy of the result turns upon the interpretation of the lowest three frequencies, requiring that the significant Raman lines should be present and that the correct weight should be assigned to each. The total 2.4 E.U., should not be in error by more than 0.5 E.U. For other molecules, for which Raman data are not available, the vibrational contribution may be based upon estimated frequencies of probable fundamental vibrations, in this case of course with somewhat higher probable error. Eventually, as our knowledge of internal vibrations increases, and the number of accurately known entropies becomes sufficiently large, it should be possible to make rapid estimates of vibrational entropy from the size and general shape of the molecule.

TABLE I. *Vibrational entropy of acetone.*

(cm^{-1})	Probable Motion	m	S
390	Central C, ⊥ to CCCO plane	1	1.00
520	Waving of methyl groups	1	0.60
770	Stretching of C−C bonds	2	0.45
1000	Twisting of molecule, mainly bending C=O bond	1	0.10
1200	Bending of CH bond	5	0.20
1450	Bending of CH bond	5	0.04
1700	Stretching of C=O bond	1	—
2900	Stretching of C−H bond	6	—
	Totals	22	2.39

For the moment of inertia of the methyl group, the value 0.0517×10^{-38} has been employed. Other moments are estimated, based upon the following interatomic distances (in Angstrom units): C−C, 1.52; C−H, 1.08; C−O, 1.4; C=O, 1.3; C=C, 1.4. The angle between the oxygen valences in methyl alcohol is taken as 100°, and between single carbon valences as 110°. Since the moments enter as the square roots into the rotational entropy, considerable errors could be made without too large effects upon the final results. In estimating the moments of the molecule as a whole, the hydrogens of the methyl group have been taken arbitrarily as a mass of three at a point 0.37 Angstrom units from the carbon atom. The principal axes are evident by inspection in the more symmetrical molecules. For methyl alcohol they were estimated to be inclined at 1° 23′ and 91° 23′ to the CO bond. The angle of inclination to the C=C bond in trimethylethylene was calculated to be 28° 20′. An error of a few degrees in the inclination of the axes produces little error in the result.

The entropies for comparison with experimental data have been calculated for the gaseous state at one atmosphere pressure and 25°C. Introducing these quantities into Eqs. (1) and (2) and combining, we obtain for the total practical entropy,

$$S_{298}(g)=23.75+\tfrac{3}{2}R\ln M+\tfrac{1}{2}R\ln A^aB^bC^c\cdots G^g$$
$$+8.70n-R\ln\sigma+S\text{ vib.}\quad(4)$$

In this equation M is the molecular weight, and A, B, etc., now represent the moments of inertia multiplied by 10^{38}.

The results of the calculations are shown in Table II, in which the first column gives the substance, the second the number of rotational degrees of freedom, the third the moments of inertia ($\times10^{38}$) the fourth the symmetry number, the fifth the sum of the translational and rotational contributions, the sixth the estimated vibrational entropy, and the seventh the total calculated entropy according to Eq. (4). In the eighth col-

[2] Dadieu and Kohlrausch, Ber. **63**, 251 (1930).
[3] Dennison, Rev. Mod. Phys. **3**, 280 (1931).
[4] Cross and Van Vleck, J. Chem. Phys. **1**, 350 (1933).

TABLE II. *Entropy of polyatomic molecules.*

Substance	n	A, B, etc.	σ	S_{tr} $+S_{rot}$	S vib	$S(g)$ 298	$S(l)$ exp.	$S_{vap.}$	$S(g)$ exp.
Methyl alcohol	4	0.301, 0.016, 0.317, 0.0517	3	57.3	0.3	57.6	30.3	26.4	56.9
Toluene	4	1.593, 3.423, 4.977, 0.0517	6	68.8	7.5	76.3	52.4	23.3	75.7
Dimethyl ether	5	0.636, 0.159, 0.795, 0.0517	18	64.5	1.1	65.6			
Acetone	5	0.846, 0.851, 1.697, 0.0517	18	67.9	2.4	70.3	47.9	21.2	70.1
Isobutane	6	1.71, 0.298, 0.0517	81	68.9	3.0	71.9	(51.5)	19.8	71.3
Trimethylethylene	6	2.364, 0.905, 3.269, 0.0517	27	75.2	3.9	79.1	59.5	20.2	79.7
Neopentane	7	1.71, 0.0517	729	74.1	4.4	78.5	(57.)	19.9	76.9

umn is shown the experimental entropy of the liquid, in the ninth, the estimated entropy of vaporization, and in the tenth the total entropy of the gas, based on the experimental data.

The experimental entropies shown in the eighth column have been taken from Parks and Huffman.[5] Those in parentheses are estimates from the measured values for closely related compounds. The entropies of vaporization of methyl alcohol and toluene are obtained from the heats of vaporization used by these authors. The heat of vaporization of acetone is taken from *International Critical Tables*.[6] The values for the vaporization of the hydrocarbons have been calculated by means of the Kistiakowsky equation. The vapor pressure data of Whitmore and Fleming[7] on neopentane give a value about one entropy unit lower than the one in column nine of the table. In view of the large variation in heats of vaporization from different sources, apparently equally reliable, it is difficult to fix the entropy of vaporization within two entropy units. For this reason, in order to be consistent, the Kistiakowsky equation was employed. The probable error in the calculated value is of the order of one entropy unit, that of the "experimental" value two entropy units.

The effect of the rotating methyl groups may be seen by comparing the result for acetone (70.3 E.U.) with a calculation which assumes that no such rotation occurs, and predicts the value 63.0.

A check on the dimethyl ether calculation, for which no experimental data are available, is obtained by means of the reaction,

$$2\,CH_3OH(g) = CH_3OCH_3(g) + H_2O(g),$$

for which Parks and Huffman find $\Delta S = 5.1$. From the calculated entropy values of Table II, together with the entropy of water vapor as given by Giauque and Ashley[8] (45.17), we obtain for the above reaction, $\Delta S = 4.4$.

With the exception of trimethylethylene, the calculation leads in every case to a value slightly higher than the corresponding experimental or estimated value. It is possible, but improbable, that this might be the result of omitting some factor from Eq. (4). It is more probable that it arises from the low temperature extrapolation employed with the experimental data. For practical purposes, the agreement is well within the limits of error.

[5] Parks and Huffman, *Free Energies of Some Organic Compounds*. Chemical Catalog Co., Inc., 1932.
[6] International Critical Tables, Vol. 5, p. 137.
[7] Whitmore and Fleming, J. Am. Chem. Soc. **55**, 806 (1933).
[8] Giauque and Ashley, Phys. Rev. **43**, 81 (1933).

The Solution of Problems Involving Permutation Degeneracy

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Matrix methods are developed for calculating the energy levels of many electron systems. These methods are based on the intimate relation between the energy matrix and the irreducible representations of the symmetric permutation group. Part I deals with the "pure matrix method," which involves explicit calculation of the matrices representing the permutations. The permutation matrices are given for states of various multiplicities arising from configurations of eight or fewer electrons. From these we obtain a very convenient orthogonal representation of the energy matrix. In particular, for symmetrical polyatomic molecules, it is shown that correct labelling of the orbits leads directly to a partial factorization of the secular determinant. A systematic procedure is given for determining just how this factorization can be achieved. Part II takes up the "algebraic method," which makes use of algebraic relations satisfied by the permutations. Explicit representations of the permutations are not required if this method is employed. The procedure is illustrated by the four electron problem, including non-orthogonality corrections. The interactions between configurations can also be calculated by the algebraic method. For symmetrical polyatomic molecules, the group of symmetry operators which commute with the Hamiltonian function can be used to obtain the secular equation in a factored form. The factorization is complete in the group theory sense. A number of illustrative examples are worked out, the energy levels of all multiplicities being found for the hexagonal (benzene) configuration, the configuration of eight similar orbits at cube corners, and the body-centered cube. The singlet levels of the tetrahedral (methane) configuration are also given.

§1. INTRODUCTION

TWO types of attack have been developed for calculating energy levels in problems involving permutation degeneracy. The more commonly employed, the wave method, is based on the use of Slater wave functions, or of "bond eigenfunctions." The second type, comprising the matrix methods, is based upon the fact that the portion of the Hamiltonian function arising from a single configuration of n non-identical electrons and having a given characteristic value, S, of the total spin, is of the form[1]

$$H=\Sigma_P H_P P. \qquad (1)$$

Here the permutation integrals, H_P, are numerical constants, and the matrices P are irreducible representations of the elements of the symmetric permutation group of n objects. The particular irreducible representation to be used is determined by the value assigned to S. The modifications of (1) required when pairs of orbits are identical, as well as the extension of the method to include interactions between configurations, have been treated by the writer in a previous paper,[2] which will be referred to as I.

The fundamental equation, (1), can be employed in a variety of ways. The most direct method, of course, is to calculate the matrices P explicitly and solve the resulting secular determinant. This will be termed the "pure matrix method." It has been discussed in I, and will be further considered in Part I of this paper.

Instead of actually calculating the P's, as contemplated in the pure matrix method, one may utilize the Dirac vector model, which expresses the P's in terms of spin variables. This vector model has been very ingeniously applied by Van Vleck to problems of complex and molecular spectra and of ferromagnetism.[3] Of course, if it were actually necessary to find the matrices representing the spin variables, the distinction between the pure matrix method and the vector model would be entirely trivial. However, as Van Vleck has shown, many problems can be solved very simply by use of algebraic relations satisfied by the spins. Van Vleck's method may accordingly be more properly classified as an algebraic, rather than as a pure matrix one, the elements of the algebra being the electronic spin vectors.

Much the same sort of simplification can be achieved by considering the algebra whose ele-

[1] P. A. M. Dirac, *The Principles of Quantum Mechanics*, Chapter XI; E. Wigner, Zeits. f. Physik **40**, 883 (1927).
[2] R. Serber, Phys. Rev. **45**, 461 (1934).
[3] J. H. Van Vleck, Phys. Rev. **45**, 405 (1934); *The Theory of Electric and Magnetic Susceptibilities*, Chapter XII.

ments are the permutations P. The use of this algebra, which will be discussed in Part II of this paper, is more convenient than the use of the spin algebra when permutations of higher order than simple interchanges are involved, or when group theory can be employed to factor the secular determinant.

Before proceeding with the applications of (1), a brief description will be given of some results of the theory of the symmetric permutation group which are of particular importance in our work.[4]

§2. The Primitive Characters of the Symmetric Permutation Group

The usual cyclic notation for the permutations will be employed.[5] Thus, I is the identity element, (12) represents the interchange of orbits one and two, (123) the permutation which replaces orbit one by two, two by three, and three by one, and so forth. The primitive character of a permutation belonging to the class specified by the partition[6] $a_1+a_2+\cdots+a_\rho=n$, for any given irreducible representation of the symmetric permutation group, will be denoted by $[a_1a_2\cdots]$, only the a's different from unity being written down. Thus the primitive character of (12) is written [2], while that of (123)(45) is written [32]. The primitive character of the identity element will be symbolized by $[I]$. It should be borne in mind that the primitive character of a permutation P is simply the spur of the matrix representing P, and is the same for all permutations belonging to a given class.

The primitive characters of the P's appearing in (1) are given by the following rule:[7]

The primitive character of a permutation belonging to the class $a_1+a_2+\cdots+a_\rho=n$ is the coefficient of x^k in

$$(-1)^{n-\rho}(1-x)(1+x^{a_1})(1+x^{a_2})\cdots(1+x^{a_\rho}),$$

where $k=\frac{1}{2}n-S$. The explicit appearance in this formula of S, the characteristic value of the total spin, is a consequence of the fact that the value assigned to S determines the particular irreducible representation to be used in (1).

It follows immediately from this rule and (1) that the number of states of multiplicity $2S+1$ arising from a configuration of n non-identical orbits is

$$[I]=\binom{n}{k}-\binom{n}{k-1}. \tag{2}$$

If the configuration contains r pairs of identical orbits, n in this formula must be replaced by $n-2r$.

I. THE PURE MATRIX METHOD

§3. The Irreducible Representations of the Permutation Group for $n\leq 8$

The matrices P, representing the permutations, have been calculated for the singlet states of an eight electron system by the method described in *I*. The results for a number of simple interchanges, i.e., permutations of the form (12), are listed on the following page. The interchanges (12), (34), (56) and (78) are diagonal in the representation we have employed, hence it suffices simply to list their characteristic values. The interchanges which are not tabulated can very easily be obtained from the ones we have given. For example, (23) can be found by use of the relation (23)=(12)(13)(12), which, in view of the diagonal form of (12), tells us how to obtain (23) simply by changing certain signs in (13). Similar relations, involving only changes in sign, suffice to determine all the remaining interchanges. Any permutation of higher order can of course be written as a product of interchanges.[8]

The representation has been so chosen that the matrices P for $n<8$ can also be read directly from the ones given. The interchanges corre-

Characteristic Values of the Diagonalized Interchanges

	States													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
(12)	−1	−1	−1	1	−1	1	−1	−1	1	−1	−1	1	−1	1
(34)	−1	−1	1	−1	−1	1	−1	1	−1	−1	1	−1	−1	1
(56)	−1	−1	−1	−1	−1	−1	1	1	1	−1	−1	−1	1	1
(78)	−1	−1	−1	−1	−1	−1	−1	−1	−1	1	1	1	1	1

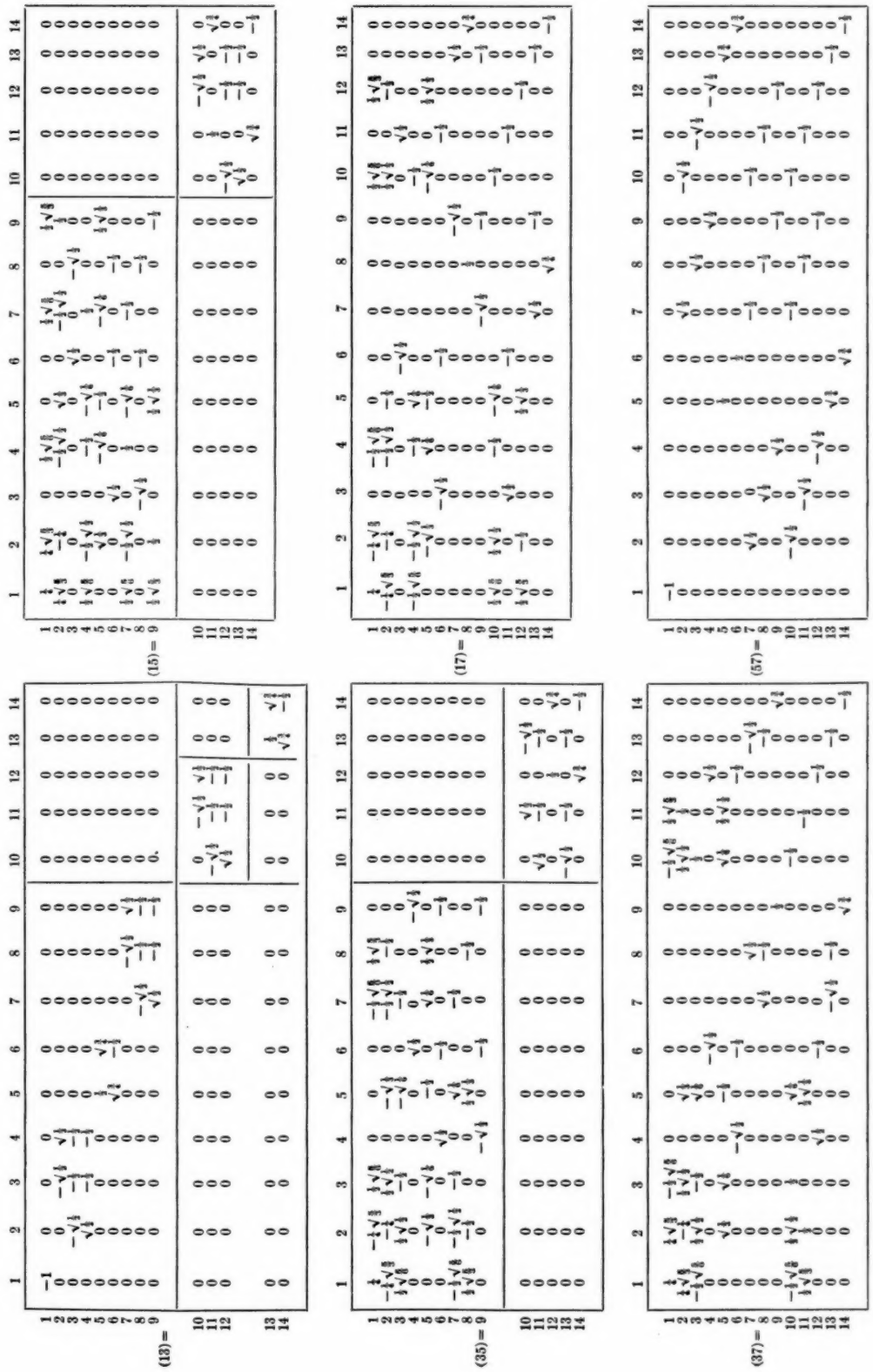
[4] For a more complete account of the theory of this group, the reader is referred to E. Wigner, *Gruppentheorie*, Chapter XIII.

[5] E. Wigner, reference 4, p. 134.

[6] E. Wigner, reference 4, p. 135.

[7] E. Wigner, reference 4, pp. 149, 196.

[8] In taking the product of two permutations, PP', the convention we adopt is that P' operates first on any function of the orbits. For example, (12)(23)=(123).


(15) =
(17) =
(57) =
(13) =
(35) =
(37) =

sponding to $n=7$, $S=\frac{1}{2}$ are identical with those for $n=8$, $S=0$ if all interchanges referring to orbit 8 are omitted. Such a relation always holds between the representations for n, $S=0$ and those for $n-1$, $S=\frac{1}{2}$. It will be observed that each of the fifteen interchanges involving only orbits one to six factors into two parts. The larger, containing states one to nine, gives the representation for $n=6$, $S=1$. The smaller, containing the last five states, gives the representation for $n=6$, $S=0$. Similarly, for the six interchanges involving only orbits one to four, the representations for $n=6$, $S=0$ factor into the representations for $n=4$, $S=1$, and for $n=4$, $S=0$, the former corresponding to states 10, 11, 12, the latter to states 13 and 14.

Substitution of any of these representations of the P's into (1) leads to an orthogonal representation of the energy matrix, i.e., if permutation integrals of unity are neglected, W and the Coulomb integrals appear in the secular determinant only on the main diagonal. The representations of H obtained in this way have several advantages over the orthogonal representations used by Eyring and his co-workers.[9] For one thing, the energy matrix is normalized, and the very convenient spur theorem can consequently be employed. Also, our representation is well adapted to the use of perturbation theory when electron pair bonding is nearly a good approximation, e.g., for $n=8$, $S=0$, when four exchange integrals are much larger than all the others. This follows from the fact that (12), (34), (56), (78) are all diagonal, hence, if the orbits are labelled so that the large exchange integrals are H_{12}, H_{34}, $\cdots$, only small terms appear off the diagonal. It should be noted that state 14 corresponds to pure electron pair bonding, (12), (34), (56) and (78) all being 1 for this state, and the average value of all other interchanges being $-\frac{1}{2}$. It is essential to have (12), (34) $\cdots$ diagonal in considering the interactions between configurations if pairs of orbits of any configuration are identical. And finally, as will be shown in the following section, partial factorization of the secular determinant can readily be obtained for symmetrical molecules. Taylor, Eyring and Sherman[9] have pointed out that for such molecules correct labelling of the orbits sometimes leads to factorization. The use of our representations greatly increases the possibilities along this line, and in addition a systematic method is afforded for determining how the factorization may be achieved.

[9] H. S. Taylor, H. Eyring and A. Sherman, J. Chem. Phys. **1**, 68 (1933); H. Eyring and G. E. Kimball, J. Chem. Phys. **1**, 239 (1933).

§4. Symmetrical Molecules

In dealing with symmetrical molecules, the secular determinant can usually be factored if a little attention is paid the group of symmetry operations (rotations and reflections) which commute with the Hamiltonian function. For a single configuration of similar orbits, these symmetry elements form a subgroup of the symmetric permutation group. It should be noted that by "permutation" we always mean a permutation of the orbits. It we were thinking of permutations of the coordinates, the remark that the elements of a subgroup of such permutations commute with the Hamiltonian function would be entirely trivial, as, in fact, all permutations of the coordinates commute with the Hamiltonian function. However, the situation is very different when we refer to permutations of the orbits, since it is obvious from (1) that permutations of this type in general do not commute with H. The existence, in a particular problem, of certain permutations which do, is consequently a real aid. When interactions between configurations must be considered, symmetry elements may correspond to permutations of the configurations among themselves, as well as to permutations of orbits within a configuration.

The procedure to be followed can best be explained by reference to a specific example. Let us consider the model of the benzene molecule consisting of six similar orbits placed at the vertices of a regular hexagon. The symmetry operations form the holohedral hexagonal group D_{6h}. However, since inclusion of the inversion element leads to no added simplification, it is sufficient to consider only the twelve elements of the hemohedral group, D_6. The primitive characters for this group may be found in Mulliken's convenient tables.[10] We shall follow Mulliken's terminology for the irreducible representations; thus the let-

[10] R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

ters A and B are used for irreducible representations of the first degree, E and T for representations of the second and third degrees, respectively. The classes will be labelled C_1, C_2, $\cdots$ in the order in which they appear in Mulliken's tables.

Proceeding around the hexagon in a clockwise direction, denote the orbits by 1,6,4,2,5,3. Each symmetry operation is evidently equivalent to a permutation of the orbits. For example, a clockwise rotation through $\pi/3$ around the sixfold axis induces the permutation (164253), while a rotation through π about the line through 1 and 2 induces the permutation (36)(45). A typical element of each class is: C_1, I; C_2, (12)(34)(56); C_3, (145)(623); C_4, (164253); C_5, (36)(45); C_6, (16)(34)(25).

Consider first the singlet states. The irreducible representation of the symmetric permutation group corresponding to $n=6$, $S=0$ is, of course, a reducible representation of the group D_6. The character in this representation, $\chi(C_i)$, of an element of C_i is given by the rule of §2. Thus $\chi(C_1)=[\mathrm{I}]=5$, $\chi(C_2)=[222]=3$, $\chi(C_3)=[33]=2$, $\chi(C_4)=[6]=0$, $\chi(C_5)=[22]=1$, $\chi(C_6)=[222]=3$. The number of times each irreducible representation of D_6 appears in our fifth degree representation of the symmetric permutation group can now be determined in the usual way.[11] One finds that A_1 appears twice, B_2 and E^* each once.

We shall not attempt to obtain immediately complete factorization of the secular determinant into a quadratic factor and three linear factors, but content ourselves with the partial factorization which results directly from the fact that (12), (34) and (56) are diagonal. It will be observed that the scheme of labelling orbits we have employed diagonalizes the symmetry element (12)(34)(56), belonging to C_2. Relabelling the orbits in any way of course corresponds to a canonical transformation of the energy matrix, the transformation matrix being simply the representation of the permutation which changes the old labelling scheme into the new one. Since the square of (12)(34)(56), is unity, its characteristic values are ± 1. Referring to the values given in Mulliken's table for the primitive characters $\chi^j(C_2)(j=A_1, B_2, E^*)$ of an element of C_2, we see that (12)(34)(56) must be 1 for the states $^1A_1$ and $^1E^*$, and -1 for $^1B_2$. The superscript indicates the multiplicity, $2S+1$. Since the secular determinant can have no matrix elements between states having different characteristic values of (12)(34)(56), it consequently factors into a linear factor, corresponding to $^1B_2$, and a quartic, containing the remaining levels. Reference to the explicit representations of (12), (34), and (56) given in §3 shows that (12)(34)(56) is -1 for state 10, which therefore is $^1B_2$, and 1 for states 11,12,13, and 14, which thus give rise to the quartic. We shall write α for exchange integrals of the type H_{16}, β for the type H_{14}, γ for the type H_{12}. Higher order permutation integrals will be neglected. Setting up the secular determinant, we find the energy of the $^1B_2$ state is, omitting the Coulomb term, $^1B_2=-3\gamma$, and the quartic is

$A-W$	$-C$	$-C$	$-\sqrt{3}C$
$-C$	$A-W$	C	$\sqrt{3}C$
$-C$	C	$A-W$	$\sqrt{3}C$
$-\sqrt{3}C$	$\sqrt{3}C$	$\sqrt{3}C$	$B-W$

with $A=-\alpha-\beta-\gamma$, $B=-3\alpha-3\beta+3\gamma$, $C=\alpha-\beta$. A double root of this equation is obviously given by $A-W=C$. Hence $^1E^*=-2\alpha-\gamma$. The energies of the $^1A_1$ levels can now be found by use of the spur theorem. The sum of the $^1A_1$ energies is found by subtracting the known energies of the remaining levels from Sp H. Similarly the sum of the squares of the $^1A_1$ level is found by subtracting the squares of the known energies from Sp H^2. The energies of the $^1A_1$ levels are then given by

$$W=\tfrac{1}{2}a\pm\tfrac{1}{2}(2b-a^2)^{\frac{1}{2}}, \tag{3}$$

where a is the sum of the energies, b is the sum of their squares. We find

$$^1A_1=-\alpha-3\beta+\gamma\pm[9(\alpha-\beta)^2+4(\alpha-\gamma)^2]^{\frac{1}{2}}. \tag{4}$$

This result has previously been obtained by Seitz and Sherman.[12]

Examining the typical elements of the classes, we see that by suitable labelling of the orbits it would alternatively be possible to make an element of C_5 or an element of C_6 diagonal. The latter choice would factor out a $^1E^*$ level, since

[11] E. Wigner, reference 4, p. 95.

[12] F. Seitz and A. Sherman, J. Chem. Phys. 2, 11 (1934).

$\chi^{E^*}(C_6)=0$, and hence (12)(34)(56) has the value 1 for one $^1E^*$ level, -1 for the other. The former choice leads to a quadratic factor, containing $^1B_2$ and $^1E^*$, and a cubic factor.

Joint use of two or more labelling schemes is often helpful, since some levels may be most easily found by using one scheme, some by using another.

§5. Cubic Configuration

As another example, consider the configuration of eight similar orbits located at the corners of a cube. Proceeding clockwise around the top face of the cube, label the orbits by the numbers 1,6,2,5. Label the orbits directly under these by 7,4,8,3, respectively. The forty-eight symmetry operations form the cubic holohedral group, O_h. Typical elements of the interesting classes are: C_2, (12)(34)-(56)(78); C_4, (17)(28)(36)(45); J, (18)(27)(36)(45); JC_2, (17)(28)(35)(46); JC_4, (12)(78). Any of these elements may be diagonalized by suitable labelling of the orbits. The choice we have made diagonalizes (12)(34)(56)(78) of class C_2, and (12)(78) of class JC_4. The energy matrix can accordingly have nonvanishing elements only between states for which both of these symmetry elements have the same characteristic values.

The irreducible representations of O_h to which the fourteen singlet states belong, together with the number of times each appears, are: A_1 (3 times), E (twice), T_2 (once), JA_1 (once), JT_2 (once). From the table of primitive characters for O_h we see that the characteristic values of our diagonal symmetry elements corresponding to these representations are

	A_1	E	T_2	JA_1	JT_2
(12)(34)(56)(78)	1	1, 1	1, −1, −1	1	1, −1, −1
(12)(78)	1	1, −1	1, −1, 1	−1	−1, −1, 1

There is an ambiguity in the columns for T_2 and JT_2 which cannot be settled by reference to the table of primitive characters alone; namely, we are uncertain which of the values in the first row correspond to which in the second row. For example, the correct assignment for one of the $^1T_2$ states may be (12)(34)(56)(78)=1, (12)(78)=1, the corresponding values for the second state may be $-1,-1$, and for the third state $-1,1$. But it is equally possible that the values for the first state should be $1,-1$, and for the second and third states $-1,1$. This question can only be settled by reference to the actual representations of the permutations given in §3. From the matrices there given, we see that the characteristic values of the symmetry elements for the states of this representation (labelled "Initial States") are

(12)(34)(56)(78)	(12)(78)	Initial States	Final States
1	1	1, 2, 5, 8, 12, 14	$^1A_{1a}$, $^1A_{1b}$, $^1A_{1c}$, ^1E_a, ^1E_b, $^1T_2$
1	−1	6, 9, 11, 13	$^1JA_1$, ^1E_a, ^1E_b, $^1JT_2$
−1	1	3, 7	$^1T_2$, $^1JT_2$
−1	−1	4, 10	$^1T_2$, $^1JT_2$

Thus the secular determinant breaks up into two identical quadratics, a quartic, and a sixth degree factor. The last column gives the irreducible representations corresponding to the various roots of these factors. The subscripts a,b,c have been introduced to distinguish between the three different $^1A_1$ levels and the two different ^1E levels. This identification of the levels follows from a comparison of the table just given with the preceding one. Consistency of the two tables requires us, for T_2 and JT_2 of the first table, to put into correspondence with each number in the first row the number directly beneath it in the second row.

The quartic factor can be handled in the same way as the quartic encountered in the preceding

section. Three roots of the sixth degree factor will then be known. The secular equation satisfied by the remaining roots, the three $^1A_1$ levels, can consequently be determined by using the three invariants Sp H, Sp H^2, Sp H^3. The equation can be written

$$W^3-aW^2+\tfrac{1}{2}(a^2-b)W-\tfrac{1}{6}(a^3-3ab+2c)=0, \tag{5}$$

where a is the sum of the three roots, b is the sum of their squares, and c is the sum of their cubes.

We shall not carry out the explicit calculations here, since the problem will be discussed in Part II by a different method.

II. THE ALGEBRAIC METHOD

§6. The Four Electron Problem, Including Non-Orthogonality Corrections

In order to illustrate the workings of the algebraic method we shall, as a first example, discuss the energies of the singlet states of four electrons in non-identical orbits. The orbits need not be orthogonal, accordingly two kinds of non-orthogonality corrections must be considered. The first kind, due to the nonvanishing values of exchange and higher order permutation integrals of unity, will play no rôle in our formal procedure, for, as Van Vleck has pointed out,[3] the most convenient way of treating this correction is to disregard it completely in obtaining formulas for the energy levels, which subsequently can easily be modified to allow for the correction. The second type of correction requires us to retain in (1) third and higher order permutation integrals. The Hamiltonian function (1) thus takes the form

$$\begin{aligned}H=&H_{12}(12)+H_{13}(13)+H_{14}(14)+H_{23}(23)+H_{24}(24)+H_{34}(34)+H_{123}[(123)+(132)]\\&+H_{124}[(124)+(142)]+H_{134}[(134)+(143)]+H_{234}[(234)+(243)]+H_{(12)(34)}(12)(34)\\&+H_{(13)(24)}(13)(24)+H_{(14)(23)}(14)(23)+H_{1234}[(1234)+(1432)]+H_{1243}[(1243)+(1342)]\\&+H_{1324}[(1324)+(1423)].\end{aligned} \tag{6}$$

In writing (6), we have omitted the Coulomb integral H_I, which contributes only an additive term to the energy, and, since without loss of generality we may suppose the permutation integrals are real, we have set $H_P=H_{P^{-1}}$. Using the rule given in §2 we find for the primitive characters $[I]=2$, $[2]=0$, $[3]=-1$, $[22]=2$, $[4]=0$. The spur of H is obtained by replacing each permutation in (6) by its primitive character; we thus find

$$\text{Sp } H=-2(H_{123}+H_{124}+H_{134}+H_{234})+2(H_{(12)(34)}+H_{(13)(24)}+H_{(14)(23)}).$$

In a similar way the spur of H^2 can be found by squaring (6) and then replacing each permutation by its primitive character. In squaring (6) it is of course unnecessary to actually multiply out term by term, for many of the resulting terms will be of a similar type. For example, the term $H_{12}(12)$ is typical of the first six terms of (6), and the contribution of interchanges to Sp H^2 can be determined by examination of the product Sp $H_{12}(12)H$. The first term of this product gives $H_{12}^2[I]$, the second is $2H_{12}H_{13}[3]$. The factor 2 is included since each cross-term appears twice in taking the square. It should be noted in this connection that the class to which the product of two permutations belongs is unchanged if the product is taken in the reverse order, as is shown by the relation $P_b(P_aP_b)P_b^{-1}=P_bP_a$. The third, fourth and fifth terms of the product are of the same type as the second, since in each case one integer in the first permutation is repeated in the second. The sixth term, however, is of a different type, and gives $2H_{12}H_{34}[22]$. Collecting the above results we see that, aside from higher order permutation integrals, the spur of H^2 is

$$2[H_{12}^2+H_{13}^2+\cdots]-2[H_{12}H_{13}+H_{12}H_{14}+\cdots]+4[H_{12}H_{34}+H_{13}H_{24}+\cdots].$$

Continuing the multiplication of Sp $H_{12}(12)H$, the next two terms are of the type $2H_{12}H_{123}(2[2])$, and the following two of the type $2H_{12}H_{134}(2[4])$. Terms involving products of double and triple

permutations consequently vanish. After completing the $H_{12}(12)$ product, we begin with $H_{123}[(123)+(132)]$, which need be multiplied only the by terms in H which follow the interchanges, since products with interchanges have already been considered. Proceeding in this way, all terms of the spur are readily obtained. Knowing Sp H and Sp H^2 the energy levels can be found by using (3). This formula of course does not include non-orthogonality corrections of the first kind mentioned above.

In our case, (3) leads to the result

$$W=-(H_{123}+H_{124}+H_{134}+H_{234})+(H_{(12)(34)}+H_{(13)(24)}+H_{(14)(23)}) \pm\{\tfrac{1}{2}[(\alpha-\beta)^2+(\alpha-\gamma)^2+(\beta-\gamma)^2]\}^{\frac{1}{2}} \quad (7)$$

with $\alpha=H_{12}+H_{34}+2H_{1324}$, $\beta=H_{13}+H_{24}+2H_{1234}$, $\gamma=H_{14}+H_{23}+2H_{1243}$. Slater[13] has obtained this formula by use of the wave method.

The method of obtaining the energy levels illustrated above is, of course, applicable whatever the number of electrons, and whatever the degree of the resulting secular determinant. However, unless other simplifying factors enter, the practical scope of the method is limited to secular problems of small degree, since for a secular problem of degree t it is in general necessary to evaluate t invariants, the spurs of H, H^2, $\cdots H^t$. If t is at all large, the pure matrix method of solving (1) is likely to afford a less tedious attack. Fortunately, simplifying factors do enter in important classes of problems. Such simplifications are usually due to the existence of symmetry elements, in addition to permutations of the coordinates, which commute with the Hamiltonian function. Cases of this sort arising in molecular spectra will be discussed in §§8 to 11. In complex spectra, some of the roots of the secular determinant will be already known since they may be obtained by the method of diagonal sums. The number of invariants we are required to compute is consequently greatly reduced. However, in such problems it is imperative to include the interactions between configurations. These will be considered in the following section.

§7. Interactions between Configurations

If we wish to consider interactions between configurations, or if the orbits of a configuration are not all different, (1) must be replaced by the more general formula

$$H^{R_iR_j}=\sqrt{2}^{-r_i-r_j}\Sigma_P H^{R_iR_j}{}_P P. \quad (8)$$

Here $H^{R_iR_j}$ is the portion of the energy matrix in which the states arising from the configuration R_i, which has r_i pairs of identical orbits, intersect the states arising from the configuration R_j, which has r_j pairs of identical orbits. It should be understood that in (8) we may have $i=j$. Eq. (8) differs in two respects from the corresponding equation, (13), given in I. The summation in (8) is over all permutations, rather than only over a subset, as in (13). This accounts for the appearance of the normalization factor $\sqrt{2}^{-r_i}$, instead of $\sqrt{2}^{r_i}$. And the P's themselves appear in (8), rather than the matrices $P^{R_iR_j}$, from which were omitted rows and columns corresponding to states which vanish in virtue of the identity of pairs of orbits. The inclusion of these rows and columns in (8) does no harm, for an obvious modification of the argument following (10) of I shows that the elements of the rows and columns so included are all zero, and hence will in no way affect the values of our spurs.

Instead of using the expression (8) for the energy matrix, $H^{R_iR_i}$, of a configuration having r_i pairs of identical orbits, it is simpler to use (1) for the configuration of $n-2r_i$ electrons obtained by omitting the identical pairs, replacing, however, H_I by H_I+C. The explicit equation for C, the additive constant due to paired electrons, is given in Van Vleck's paper.[3]

The spur of H^2 may be obtained from (8) and the relation

$$\text{Sp } H^2=\Sigma_{ij}\text{ Sp } H^{R_iR_j}H^{R_jR_i}. \quad (9)$$

Analogous formulas hold for the higher invariants.

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[13] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

As an illustration of the use of (8) and (9), let us find the contribution to Sp H^2 of the interaction between a configuration A, consisting of three non-identical orbits, and a configuration B, which has orbits 1 and 2 identical. All non-orthogonality corrections will be neglected. As orbits 1 and 2 of B are the same, $H^{BA}{}_{P'}=H^{BA}{}_{P}$ if $P'=(12)P$. Hence, (8) gives

$$H^{BA}=\sqrt{\tfrac{1}{2}}\{H^{BA}{}_{I}[I+(12)]+H^{BA}{}_{13}[(13)+(132)]+H^{BA}{}_{23}[(23)+(123)]\},$$
$$H^{AB}=\sqrt{\tfrac{1}{2}}\{H^{BA}{}_{I}[I+(12)]+H^{BA}{}_{13}[(13)+(123)]+H^{BA}{}_{23}[(23)+(132)]\}.$$

The second of these relations follows from the fact that H^{AB} is the matrix adjoint to H^{BA}. Since the permutations are unitary operators, H^{AB} may accordingly be obtained by replacing each permutation in H^{BA} by its reciprocal. The interaction between A and B contributes to Sp H^2 the terms

$$\begin{aligned}\text{Sp } H^{BA}H^{AB}+\text{Sp } H^{AB}H^{BA}&=2\text{ Sp } H^{BA}H^{AB}\\&=(H^{BA}{}_{I}{}^{2}+H^{BA}{}_{13}{}^{2}+H^{BA}{}_{23}{}^{2})(2[I]+2[2])\\&+2(H^{BA}{}_{I}H^{BA}{}_{13}+H^{BA}{}_{I}H^{BA}{}_{23}+H^{BA}{}_{13}H^{BA}{}_{23})(2[2]+2[3])\\&=2[(H^{BA}{}_{I}-H^{BA}{}_{13})^2+(H^{BA}{}_{I}-H^{BA}{}_{23})^2+(H^{BA}{}_{13}-H^{BA}{}_{23})^2].\end{aligned}\tag{10}$$

This algebraic solution of the problem offers an interesting alternative to the pure matrix solution given in *I* in connection with the calculation of the ^2D levels arising from the atomic configuration d^3. It is interesting to observe that if the values of the characters appropriate to $S=\frac{3}{2}$ are used in (10), the spur reduces, as it must, to zero.

§8. Symmetrical Molecules

The algebraic method is very well adapted for Heitler-London calculations of the energy levels of symmetrical polyatomic molecules, since the aid of the group of symmetry operations which commute with the Hamiltonian function can be invoked to factor the secular equation. The number and complexity of the invariants which must be evaluated are consequently greatly reduced. Consider, for example, the hexagonal configuration discussed in §4. Proceeding clockwise around the hexagon, label the orbits 1,2,3,4,5,6. The twelve symmetry operations are

$$\begin{array}{ll}C_1: \text{I} & C_4: (123456),\ (165432)\\ C_2: (14)(25)(36) & C_5: (26)(35),\ (13)(46),\ (15)(24)\\ C_3: (135)(246),\ (153)(264) & C_6: (12)(36)(45),\ (14)(23)(56),\ (16)(25)(34).\end{array}\tag{11}$$

We now introduce the operators χ_j, used by Dirac,[1] which are defined by

$$\chi_j=(1/n_j)\Sigma_{P_{c_j}}P_{c_j},$$

where the summation is over all elements in class C_j, and n_j is the number of such elements. For example $\chi_3=\frac{1}{2}[(135)(246)+(153)(264)]$. We shall call these operators "Dirac characters." They must not be confused with the ordinary characters and primitive characters, which are not operators, but spurs of matrices. The Dirac characters, χ_j, commute with all elements of the symmetry group, consequently the matrices representing them must be constants (multiples of the unit matrix) within an irreducible representation of this group. Since the spur of χ_j equals the spur of one of the elements P_{c_j}, the characteristic value of χ_j for a given irreducible representation may be obtained by dividing the primitive character of P_{c_j}, for that representation, by the degree of the representation. The characteristic values of the χ_j, for the three irreducible representations to which the singlet states belong, are given in the following table.

	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6
A_1	1	1	1	1	1	1
B_2	1	−1	1	−1	−1	1
E^*	1	1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	0

Consider a representation in which the energy matrix, H, is diagonal, and in which the matrices representing the symmetry elements are completely reduced. Since the irreducible representation A_1 occurs twice, the characteristic values of H may be written $^1A_{1+}$, $^1A_{1-}$, $^1B_2$, $^1E^*$, $^1E^*$. The corresponding characteristic values of χ_4, for example,

are 1, 1, -1, $-\frac{1}{2}$, $-\frac{1}{2}$. From the table given above we see that the characteristic values of $\frac{1}{2}(\chi_1-\chi_2)$ are 0, 0, 1, 0, 0. Hence the characteristic values of $\frac{1}{2}(\chi_1-\chi_2)H$ are 0, 0, $^1B_2$, 0, 0, and the energy of the $^1B_2$ state is simply the spur of this matrix. It follows that in any representation $^1B_2=\mathrm{Sp}\ \frac{1}{2}(\chi_1-\chi_2)H$. In a similar way we prove that the sum of the energies of the $^1E^*$ levels is $2^1E^*=\mathrm{Sp}\ (\chi_1-\chi_6)H$. The sum of the $^1A_1$ energies which we denote by $[^1A_1]$ can now be obtained from the relation $[^1A_1]+{}^1B_2=\mathrm{Sp}\ \chi_6 H$. In order to separate the $^1A_1$ levels, it is necessary to find the sum of their squares, which we write $[^1A_1{}^2]$. This can be obtained most simply by subtracting the squares of the energies of the other levels from Sp H^2. The explicit expression for $^1A_{1+}$ and $^1A_{1-}$ are then found by use of (3). It is evident that there are a variety of other ways in which the factorization of the secular determinant could be executed. Which one is chosen is solely a matter of convenience.

The calculations indicated above are readily carried out. The energy matrix, neglecting non-orthogonality corrections, and omitting the additive Coulomb term is,

$$H=\alpha\{(12)+(23)+(34)+(45)+(56)+(61)\}+\beta\{(13)+(15)+(24)+(26)+(35)+(46)\}+\gamma\{(14)+(25)+(36)\}, \quad (12)$$

with $\alpha=H_{12}$, $\beta=H_{13}$, $\gamma=H_{14}$. One readily verifies that H commutes with the symmetry elements (11).

As remarked in §6, it is by no means necessary to evaluate all the terms appearing in the various spurs. In fact, it is obvious from the symmetry of the problem that

$$\mathrm{Sp}\ \chi_j H=\mathrm{Sp}\ \chi_j\{6\alpha(12)+6\beta(13)+3\gamma(14)\}.$$

Of course $\chi_1 H$ is simply H itself. Thus

$$\mathrm{Sp}\ H=(6\alpha+6\beta+3\gamma)[2]=-6a-6\beta-3\gamma, \quad (13)$$

upon evaluating [2] by means of the rule given in §2, while

$$\mathrm{Sp}\ \chi_2 H=\mathrm{Sp}\ (14)(25)(36)\{6\alpha(12)+6\beta(13)+6\gamma(14)\}=6\alpha[42]+6\beta[42]+3\gamma[22]=-6\alpha-6\beta+3\gamma, \quad (14)$$

and

$$\mathrm{Sp}\ \chi_6 H=\mathrm{Sp}\ \tfrac{1}{3}\{(12)(36)(45)+(14)(23)(56)+(16)(25)(34)\}\{6\alpha(12)+6\beta(13)+3\gamma(14)\}=2\alpha\{[22]+2[42]\}+2\beta\{3[42]\}+\gamma\{2[42]+[22]\}=-2\alpha-6\beta-\gamma. \quad (15)$$

Half the difference of (13) and (14) gives $^1B_2=-3\gamma$ and half the difference of (13) and (15) gives $^1E^*=-2\alpha-\gamma$. The sum of the $^1A_1$ levels is then found to be $[^1A_1]=-2\alpha-6\beta+2\gamma$.

Let A, B, C be the coefficients of α, β, γ in (12). In finding Sp H^2 it is sufficient to write

$$H^2=\{6\alpha(12)+6\beta(13)+3\gamma(14)\}\{\alpha A+\beta B+\gamma C\}=6\alpha^2(12)A+6\beta^2(13)B+3\gamma^2(14)C+12\alpha\beta(12)B+12\alpha\gamma(12)C+12\beta\gamma(13)C.$$

As we will require Sp $\chi_5 H^2$ in finding the triplet levels, we shall not lump together all permutations belonging to the same class, but develop H^2 in a more complete form suitable for multiplication with a χ. Since only products of H^2 with χ's are of interest, the abbreviated form of multiplication given above is still permissible. Thus, beginning the multiplication of $(12)A$, the first term is I, the second is (123), and the third is (12)(34). The fourth term, (12)(45), must be considered of a different type than the third in spite of the fact that it belongs to the same class, for referring to a diagram of the hexagon, we see that vertices 4 and 5 are diagonally opposite 1 and 2, while 3 is opposite neither. The fifth term, (12)(56) is evidently of the same type as (12)(34), while the sixth, (162) is of the type (123). Proceeding in this way, we obtain the expression

$$H^2=6\alpha^2\{I+2(123)+2(12)(34)+(12)(45)\}+6\beta^2\{I+2(153)+2(13)(24)+(13)(46)\}+3\gamma^2\{I+2(14)(25)\}+12\alpha\beta\{2(123)+2(152)+2(12)(35)\}+12\alpha\gamma\{2(152)+(12)(36)\}+12\beta\gamma\{2(152)+(13)(25)\}. \quad (16)$$

Replacing each permutation by its character gives

$$\text{Sp } H^2 = 36\alpha^2+36\beta^2+21\gamma^2-24\alpha\beta-12\alpha\gamma-12\beta\gamma.$$

We can now substitute $a=[{}^1A_1]$, $b=[{}^1A_1{}^2]=\text{Sp } H^2-({}^1B_2)^2-2({}^1E^*)^2$ in (3) and again obtain the result (4).

The nine triplet states can be handled in the same way. The states ${}^3A_2$ and ${}^3E^*$ each occur once, ${}^3B_1$ and ${}^3E^*_*$ each twice. The only new spurs it is necessary to calculate are Sp $\chi_5 H$ and Sp $\chi_5 H^2$. The latter is needed because there are now two representations which occur twice: Sp $\chi_5 H^2$, which is readily obtained with the aid of (16), can be used to find ${}^3B_{1\pm}$, and then Sp H^2 to find ${}^3E^*_{*\pm}$. The other spurs required are obtained simply by substituting the appropriate values of the characters in (13), (14), (15), and (16). The quintet and septet energies can be obtained in a similar way from (13), (14), and (15). The energies are found to be

$$\begin{aligned}
{}^3A_2 &= -4\alpha-\gamma, & {}^3B_1 &= -(\alpha+3\beta+\gamma)\pm[5(\alpha-\beta)^2+4(\beta-\gamma)^2]^{\frac{1}{2}},\\
{}^3E^* &= -\alpha-3\beta-\gamma, & {}^3E_*{}^* &= -\tfrac{1}{2}(5\alpha+3\beta+2\gamma)\pm\tfrac{1}{2}[5(\alpha-\beta)^2+12(\alpha-\gamma)^2+4(\beta-\gamma)^2]^{\frac{1}{2}},\\
{}^5A_1 &= -2\alpha-6\beta-\gamma, & {}^5E^* &= -5\alpha-3\beta-\gamma,\\
{}^5E^*_* &= -3\alpha-3\beta-3\gamma, & {}^7B_1 &= -6\alpha-6\beta-3\gamma.
\end{aligned}$$

The method illustrated above is applicable whenever the Hamiltonian function possesses symmetry elements in addition to the permutations of the coordinates. The orthogonality relations satisfied by the primitive characters of the symmetry group assure us that complete factorization of the secular determinant can always be obtained. This method is particularly convenient when the energies of states of all multiplicities are desired, since the same expressions for the spurs are involved in all cases, only the particular values of the characters changing in passing from one value of S to another.

A very convenient running check on the calculations is afforded by noting that when all the exchange integrals are made equal the energies of all the states of a given multiplicity are the same, and are given by[3]

$${}^{2S+1}W = -\tfrac{1}{4}H_{12}[n(n-4)+4S(S+1)],$$

where H_{12} is the common value of the exchange integrals, and n is the number of electrons. Thus in the benzene problem considered above, if we put $\alpha=\beta=\gamma$ the singlet energies all reduce to ${}^1W=-3\alpha$. Sp $\chi_2 H$, which is the sum of the energies of four states minus the energy of one, must consequently reduce to $3\,{}^1W$, i.e., to -9α, while, to pick another example, Sp H^2 must become $5({}^1W)^2$ or $45\alpha^2$.

§9. Cubic Configuration

The problem considered in §5 also can be readily handled by the algebraic method. The orbits will be labelled as shown in Fig. 1. The Hamiltonian function for this configuration is

$$\begin{aligned}
H=\alpha\{&(12)+(13)+(15)+(24)+(26)+(34)+(37)+(48)+(56)+(57)+(68)+(78)\}\\
&+\beta\{(14)+(16)+(17)+(23)+(25)+(28)+(35)+(38)+(46)+(47)+(58)+(67)\}\\
&+\gamma\{(18)+(27)+(36)+(45)\}. \qquad (17)
\end{aligned}$$

The symmetry group of this Hamiltonian function is the cubic holohedral group, O_h.

There are twenty-eight triplet states; as these offer the most complicated problem, we shall treat them first. The number of times each representation of the cubic group occurs, and the corresponding characteristic values of the Dirac characters, are given in the following table.

It will be seen from this table that the determination of the energies can be carried out through the evaluation of the following spurs: Sp H, Sp $\chi_2 H$, Sp $\chi_3 H$, Sp $\chi_4 H$, Sp JH, Sp $J\chi_4 H$, Sp H^2, Sp $\chi_2 H^2$, Sp $\chi_4 H^2$, Sp JH^2, Sp H^3. In finding Sp $H^3=$Sp $\{12\alpha(12)+12\beta(14)+4\gamma(18)\}H^2$, the labor is materially shortened if we note that, since the order of multiplication is immaterial for our purposes, H^3 is of the form $(A+B+C)^3=A^3+B^3+C^3+3(A^2B+A^2C+AB^2+B^2C+AC^2+BC^2)+6ABC$. The cubic equation satisfied by the ${}^3JT_1$ levels is obtained by the use of (5).

	χ_1	χ_2	χ_3	χ_4	χ_5	J	$J\chi_2$	$J\chi_3$	$J\chi_4$	$J\chi_5$
$(2)T_1$	1	$-\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$	0	1	$-\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$	0
$(2)T_2$	1	$-\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	0	1	$-\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	0
$(2)JA_2$	1	1	−1	−1	1	−1	−1	1	1	−1
$(1)JE$	1	1	0	0	$-\frac{1}{2}$	−1	−1	0	0	$\frac{1}{2}$
$(3)JT_1$	1	$-\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$	0	−1	$\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	0
$(1)JT_2$	1	$-\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	0	−1	$\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$	0

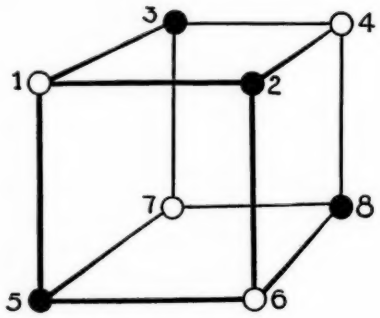

FIG. 1.

The spurs calculated in connection with the triplet levels also suffice to determine the energies of the levels of other multiplicities. Carrying out the algebra, we find

$$
\begin{aligned}
&{}^1T_2 = -4(\alpha+\beta), && {}^1E = -2(2\alpha+\beta+\gamma)\pm 2[(\alpha-\beta)^2+(\alpha-\gamma)^2]^{\frac{1}{2}},\\
&{}^1JA_1 = -2(3\alpha+\gamma), && {}^3T_1 = -(5\alpha+3\beta+2\gamma)\pm[(\alpha-\beta)^2+4(\alpha-\gamma)^2]^{\frac{1}{2}},\\
&{}^1JT_2 = -2(\alpha+2\beta+\gamma), && {}^3T_2 = -(3\alpha+5\beta+2\gamma)\pm[5(\alpha-\beta)^2+4(\beta-\gamma)^2]^{\frac{1}{2}},\\
&{}^3JE = -2(2\alpha+2\beta+\gamma), && {}^3JA_2 = -2(\alpha+4\beta)\pm\{2[7(\alpha-\beta)^2+(\alpha-\gamma)^2+(\beta-\gamma)^2]\}^{\frac{1}{2}},\\
&{}^3JT_2 = -2(3\alpha+\beta+\gamma), && {}^3JT_1 = W,
\end{aligned}
$$

$$
\begin{aligned}
W^3+2(7\alpha+7\beta+\gamma)W^2+4(13\alpha^2+14\beta^2-\gamma^2+37\alpha\beta+7\alpha\gamma+5\beta\gamma)W\\
+8(5\alpha^3+8\beta^3-\gamma^3+42\alpha^2\beta+8\alpha^2\gamma+41\alpha\beta^2+5\beta^2\gamma-2\beta\gamma^2+19\alpha\beta\gamma)=0,
\end{aligned}
$$

$$
\begin{aligned}
&{}^5JE = -2(3\alpha+3\beta+\gamma), && {}^5A_1 = -2(2\alpha+4\beta+\gamma)\pm\{2[(\alpha+\gamma-2\beta)^2+3(\alpha-\beta)^2+(\beta-\gamma)^2]\}^{\frac{1}{2}},\\
&{}^5JT_1 = -2(2\alpha+4\beta+\gamma), && {}^5E = -(7\alpha+5\beta+2\gamma)\pm[(\alpha-\beta)^2+4(\alpha-\gamma)^2]^{\frac{1}{2}},\\
&{}^5JT_2 = -2(4\alpha+2\beta+\gamma), && {}^5T_2 = -2(3\alpha+3\beta+\gamma)\pm\{2[(\alpha-\beta)^2+(\alpha-\gamma)^2+(\beta-\gamma)^2]\}^{\frac{1}{2}},\\
&{}^7A_2 = -2(3\alpha+6\beta+\gamma), && {}^7T_2 = -4(2\alpha+2\beta+\gamma),\\
&{}^7JT_1 = -2(5\alpha+4\beta+\gamma), && {}^9A_1 = -4(3\alpha+3\beta+\gamma).
\end{aligned}
$$

The cubic equation satisfied by the ${}^1A_1$ levels has been omitted from the above results, since it has already been given by Seitz and Sherman.[12]

§10. Body-Centered Cube

The addition of a ninth electron in a spherically symmetric orbit in the center of the cube simply adds to each energy level of multiplicity $2S+1$ given in the preceding section the term[3] $W_9=Q_9-\delta[(13/4)+S'(S'+1)-S(S+1)]$, where Q_9 is a Coulomb term, δ is the exchange integral between the central orbit and a corner orbit, and S' is the characteristic value of the total spin of all nine electrons. Each singlet energy level of the simple cube is thus augmented by $Q_9-4\delta$, while, for $S\neq 0$, the resultant states with $S'=S-\frac{1}{2}$ differ from their parent states by $Q_9-\delta(3-S)$. The case of eight sodium atoms at the corners of a cube has been considered by Taylor, Eyring and Sherman,[9] and by Seitz and Sherman.[12] If, following them, we use Rosen's value for the Coulomb integral, namely, 28.3 percent of the Na_2 Morse curve, we find $Q_9=8\times(28.3/71.7)\delta=3.16\delta$. Hence, since δ is negative, addition of the ninth electron raises the energies of the singlet states of the cube, but lowers the energies of states of higher multiplicity. If δ is sufficiently small, the normal state of the body-centered cube is still ${}^2A_1$, arising from the normal state, ${}^1A_1$, of the cube. For a larger value of δ, the normal state becomes ${}^2JA_2$, arising from the lowest triplet state of the cube, ${}^3JA_2$. For this state the body-centered cube will be larger than the simple cube in its normal state, since the magnitude of δ is maximized by making the distance from a corner to the center of the cube, rather than the cube edge, equal to the equilibrium distance of the Morse curve. Actually, explicit calculation shows that δ is sufficiently

large to make ${}^2JA_2$ the normal state. The numerical results will not be given here, since they are contained in a recent paper by Stearn, Lindsley and Eyring.[14]

The energies of a number of the excited states which are derived from triplet states of the simple cube are given incorrectly by the latter authors. Their formulas for the simple cube states ${}^3T_1$ (Γ_4 in their notation), ${}^3T_2(\Gamma_5)$, and ${}^3JT_1(\Gamma_9)$, which disagree with ours, are certainly in error, since they do not reduce properly in the limiting cases considered by Seitz and Sherman[12] by means of the vector model. The source of the error lies in the fact that their "method II," which they used in finding the energies of the triplet states, is incorrect when applied to irreducible representations of higher than the first degree which appear more than once in the secular determinant. Suppose, for example, that an irreducible representation of degree r ($r>1$) occurs twice, and let the corresponding wave functions be $\psi_1, \psi_2, \cdots\psi_r$, and $\psi'_1, \psi'_2, \cdots\psi'_r$. The subscript tells to which row of a particular irreducible representation of the symmetry elements, $D(R)$, the wave function belongs. This representation is of course not unique, since if S is any canonical transformation, $S^{-1}D(R)S$ is also a representation. If the subscripts in the two sets of wave functions refer to the same representation, the secular determinant will factor into r quadratics. It is clear that if a canonical transformation S is applied to the first set of wave functions, and a transformation S' is applied to the second set, the secular equation will remain in a factored form only provided $S=S'$. The formula (7) used by Stearn, Lindsley and Eyring determines the ψ_i only within a numerical factor, i.e., if we use ψ_i to denote the normalized wave functions, (7) gives $\alpha_i\psi_i$, rather than ψ_i itself. The summation involved in passing from (7) to (8) thus amounts to taking a certain linear combination of the ψ_i. Similarly, the passage from (7) to (8) leads to a linear combination of the ψ'_i, a linear combination however, which is not the same as that applied to the ψ_i. The factorization of the secular determinant is consequently destroyed, and it is not possible to obtain the energies merely by solution of the quadratic equation resulting from consideration only of the two linear combinations given by (8). The occurrence of such a difficulty might have been anticipated from the fact that the factorization of the secular determinant is contingent upon the use of a definite representation, whereas the Eq. (8) employed by Stearn, Lindsley and Eyring involves only the primitive characters, which are independent of the representation.

§11. Tetrahedral Configuration

The tetrahedral configuration exemplified by methane is equivalent to the configuration shown in Fig. 1 if orbits 1,4,6 and 7 are considered different from 2,3,5 and 8. The Hamiltonian function for this configuration is

$$\begin{aligned}H=\alpha\{&(12)+(13)+(15)+(24)+(26)+(34)+(37)+(48)+(56)+(57)+(68)+(78)\}\\&+\beta\{(14)+(16)+(17)+(46)+(47)+(67)\}+\beta'\{(23)+(25)+(28)+(35)+(38)+(58)\}\\&+\gamma\{(18)+(27)+(36)+(45)\}.\end{aligned}\tag{18}$$

It is readily shown with the aid of the vector model that the singlet energies of the tetrahedral configuration involve β and β' only in the combination $\beta+\beta'$. For, in a representation in which the resultant spins of the electrons in orbits 1,4,6 and 7, and of the electrons in orbits 2,3,5 and 8 are "good quantum numbers," with characteristic values S_1 and S_2, respectively, β and β' appear in the energy matrix only in the diagonal elements, and their contribution to these elements is[12] $-S_1(S_1+1)\beta-S_2(S_2+1)\beta'$. The singlet states of the tetrahedral configuration necessarily have $S_1=S_2$, which proves the proposition stated above. If we write (18) in the form

$$H=\alpha A+\beta B+\beta' B'+\gamma C=\alpha A+\tfrac{1}{2}(\beta+\beta')(B+B')+\gamma C+\tfrac{1}{2}(\beta-\beta')(B-B'),\tag{19}$$

it follows that the last term of (19) vanishes for the singlet states. Comparing the first three terms of (19) with (17), we see that the formulas for the singlet levels of the tetrahedral configuration may be obtained from those for the singlet levels of the cubic configuration simply by replacing β by $\frac{1}{2}(\beta+\beta')$.

[14] A. E. Stearn, C. H. Lindsley and H. Eyring, J. Chem. Phys. **2**, 410 (1934).

The Hamiltonian function (18) is invariant under the twenty-four operations of the tetrahedral group, T_d. It remains to determine to which irreducible representations of this group the singlet states belong. The symmetry of the energy matrix in β and β' introduces another symmetry element, the inversion $J=(18)(27)(36)(45)$, which, applied to (18), interchanges β and β'. The resultant group of forty-eight elements is evidently isomorphic to the cubic holohedral group, O_h. Referring to Mulliken's tables for the group T_d, we see that it differs from the cubic group O only by the inclusion of an inversion in classes C_3 and C_4. The group obtained by adding an inversion to T_d consequently differs from O_h only in that classes C_3 and JC_3, C_4 and JC_4 are interchanged. It follows immediately that the states of the cube labelled $^1A_1$, ^1E, $^1T_2$, $^1JA_1$, $^1JT_2$, correspond to the states $^1A_1$, ^1E, $^1T_2$, $^1A_2$, $^1T_1$, respectively, of the tetrahedron.

The energies of the $^1A_1$ levels of the tetrahedron have also been computed by Seitz and Sherman,[12] while Eyring, Frost and Turkevich[15] have given formulas for the singlet states. A typographical error should be noted in the latter authors' formula for $^1A_2$ (Γ_2 in their notation). Their results for $^1E(\Gamma_3)$ are also in error.

I am deeply in debt to Professor J. H. Van Vleck, both for the interest he has taken in this work, and for his kindness in criticizing the manuscript.

[15] H. Eyring, A. A. Frost and J. Turkevich, J. Chem. Phys. **1**, 777 (1933).

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The Heat Capacity Curves of the Simpler Gases, VI. A Correction

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(J. Chem. Phys. **2**, 389, 1934)

IN our paper of the above title a contribution of $R \ln 2$, resulting from the electron spin of the deuterium atom, was omitted from the free energy values of atomic deuterium, through an oversight. To correct for this omission all entries in the fourth column of Table IV (p. 392) should be increased by 1.377 units. This correction also influences Table X (p. 394). The corrected Table X is as follows:

TABLE X. *Dissociation constants and percentage dissociation of hydrogen.*

T, °K	K		
	H^1H^1	H^1H^2	H^2H^2
1000	64.49×10^{-19}	24.78×10^{-19}	37.08×10^{-19}
1500	36.00×10^{-11}	15.66×10^{-11}	26.99×10^{-11}
2000	29.60×10^{-7}	13.62×10^{-7}	24.91×10^{-7}
2500	6.915×10^{-4}	3.276×10^{-4}	6.168×10^{-4}
3000	26.87×10^{-3}	12.95×10^{-3}	24.75×10^{-3}
T, °K	Percent dissociation (1 atmosphere)		
	H^1H^1	H^1H^2	H^2H^2
1000	13×10^{-8}	7.9×10^{-8}	9.6×10^{-8}
1500	9.5×10^{-4}	6.3×10^{-4}	8.2×10^{-4}
2000	8.6×10^{-2}	5.8×10^{-2}	7.8×10^{-2}
2500	1.31	0.91	1.24
3000	8.1	5.66	7.9

Except for a portion of the discussion in the paragraph which begins five lines below Table X, no other portions of our paper are influenced by this correction.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Raman Spectra of Sulphuric Acid Solutions

A study of the Raman spectra of sulphuric acid for varying concentrations has been made by Nisi,[1] Woodward,[2] Bell and Fredrickson,[3] Rao,[4] Woodward and Horner.[5] Woodward and Horner have been the first to report a decided shift in frequency with decreasing concentration. Using the conventional set-up with a spectrograph which gave a dispersion of 15A/mm at 4300A, we attempted to check this frequency change. All plates were measured by a comparator and checked by a densitometer. The 4339 and 4916A mercury lines were used as standards. Special precautions were taken to obtain 100 percent sulphuric acid. The acid used had a F.P. of 10.3°C. All concentrations are given in volume percent. The frequency differences (cm^{-1}) for various concentrations of sulphuric acid are given in Table I (numbers in parenthesis indicate intensities; *s* means sharp lines, *b* broad). The water bands showed up clearly for 25 and 10 percent. No trace of the 1027 cm^{-1} line was found for 100 percent acid.

TABLE I.

	100%	95%	75%	50%	25%	10%
Group I (b)	363±7 (4)	395±5 (4)	417±6 (4)	425±3 (3)	425±7 (3)	433 (?)
Group II (b)	556±6 (4)	557±5 (4)	575±2 (4)	582±4 (3)	582±5 (3)	595±5 (2)
Group III (s)	905±1 (8)	906±1 (8)	909±5 (4)	887±4 (3)	887 (?)	
Group IV (s)					984±3 (6)	974±4 (7)
Group V		1027±2 (4)	1027±2 (6)	1028±2 (7)	1041±4 (6)	1041±3 (4)
Group VI	1123±9 (2)	1123±5 (2)				

The data obtained from a study of acid sulphate solutions have shown 427, 593, 979, 1051 cm^{-1} to be common frequencies,[6] with 1051 as the strongest. Sulphate solutions show 452, 617, 982, 1106 cm^{-1} as common frequencies,[7] with 982 as the most intense. Lines which appear below 50 percent and are most intense at 10 percent have been associated with $S\overline{O}_4$ ions. Those which appear at 95 percent, increase to maximum intensity around 50 percent, and then decrease, have been called $HS\overline{O}_4$ lines. Those most intense at 100 percent have been attributed to H_2SO_4 molecules. From this it would appear that in our data group IV is associated with the $S\overline{O}_4$ ion, group V with the $HS\overline{O}_4$ ion, and group VI with the H_2SO_4 molecule. This is in agreement with the results of Woodward and Horner. They, too, found an increase in frequency at lower concentrations for group V.

For the other groups, however, they found the following:

Group I: Three frequencies 381, 417, 452; with 381 strongest for 100 percent, 417 for 50 percent (due to $HS\overline{O}_4$ ion?), and 452 for 10 percent (due to $S\overline{O}_4$ ion). Both 381 and 417 were found at 100 percent, 417 and 452 at 10 percent.

Group II: Three frequencies 555, 595, 617; 555 strongest for 100 percent, 595 for 50 percent (due to $HS\overline{O}_4$ ion), and 617 for 10 percent (due to $S\overline{O}_4$ ion).

Group III: Two frequencies 910, 896; 910, 100 to 75 percent, 896, 50 to 10 percent.

For group III our results are in agreement with theirs, but in groups I and II our data seem to indicate a gradual shift in frequency, rather than a shift among three different frequencies. This gradual increase in frequency with greater dilution would seem to indicate some sort of gradual change in the molecular arrangement. It may be pointed out that groups I and II at low concentrations contain frequencies which have been found in solutions containing the $HS\overline{O}_4$ ion (427 and 593 cm^{-1}).

An attempt was made to obtain the Raman spectra of sulphuric acid solutions in anhydrous acetic acid. The results were rather unsatisfactory because of a strong continuous background. The more intense acetic acid lines (889 and 2942 cm^{-1}) were found for all concentrations. Only for 50 percent (by volume) were sulphuric acid lines obtained; these were 582 and 1028 cm^{-1}.

The anhydrous acetic acid used had a F.P. of 16.3°C. For the pure acid the following Raman lines were obtained (cm^{-1}):

$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$
24444±1 (3)	2944	22055±1 (3)	883
24408±1 (2)	2945	21767±1 (4)	2938
24079±7 (3)	626	21701±7 (1)	1294 (?)
23809±1 (1)	896	21663±7 (1)	1275
23266±7 (1)	1439	21580±1 (2)	1358 or 2936
22490±1 (1)	448	21515±2 (1)	1423
22321±1 (2)	617	21263±7 (1)	1675

We wish to thank Dr. A. W. Hutchison of the Department of Chemistry for preparing some of the solutions

used, and Dr. L. T. DeVore of the Department of Physics for densitometer measurements of some of the plates.

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August 18, 1934.

[1] Nisi, Jap. J. Phys. **5**, 119 (1929).
[2] Woodward, Phys. Zeits. **32**, 212 and 788 (1931).
[3] Bell and Fredrickson, Phys. Rev. **37**, 1562 (1931).
[4] Rao, Ind. J. Phys. **8**, 123 (1933).
[5] Woodward and Horner, Proc. Roy. Soc. **A144**, 129 (1934).
[6] Average of results obtained by Nisi, Woodward and Rao.
[7] Kohlrausch, *Der Smekal-Raman Effekt* (1931).

The Infrared Absorption Spectrum of Silane

The infrared spectrum of methane has been very extensively investigated and the normal frequencies are well known. It has been shown that the molecule has the form of a regular tetrahedron. Because of its probable similarity to methane it has seemed of interest to study the absorption in the infrared of silane (SiH_4). With an absorption cell 6 cm long fitted with rocksalt windows the spectrum has been measured to beyond 11.0μ, by using a Wadsworth spectrometer. Four bands enumerated in the order of their intensities have been located at wave-length positions 10.5μ, 4.58μ, 3.187μ and 5.2μ.

The spectrum appears to be entirely similar to that of methane, the three most intense bands definitely showing P, Q and R branches. Two of these regions, at 3.187μ and 4.58μ, have also been examined by means of an echellette grating. The first of these falls just in the water vapor absorption region at 3.16μ, which is quite intense during the summer months because of the high humidity. It has been possible by running transmission curves through the cell with and without gas, and by referring to the work of Plyler and Sleator,[1] quite successfully to separate the two, especially near the center where no intense water vapor lines exist. The Q branch is very intense and the lines in the P and R branches are separated by a spacing of about 5.5 cm^{-1}.

The 4.58μ region resembles the other at 3.187μ a great deal, showing also an extremely intense Q branch. The line separation of the P and Q branches is also about 5.5 cm^{-1} here.

By way of a comparison with the methane spectrum we submit Table I giving the frequency positions of the observed silane bands, their approximate intensities, and what we deem the corresponding frequencies for methane, using the notation of Dennison.

TABLE I. *A, observed frequencies in SiH_4 in cm^{-1}; B, intensities; C, corresponding frequencies in CH_4 in cm^{-1}; D, assignment in Dennison's notation.*

A	*B*	*C*	*D*
965	50.	1304	ν_4
1920	0.1	2600	$2\nu_4$
2183.6	20.	3014	ν_3
3155.9	1.0	4217 }	$\nu_1+\nu_4$ }
		4315 }	$\nu_3+\nu_4$ }

The band found at 3155.9 cm^{-1} might correspond either with the frequency $\nu_1+\nu_4$ or with $\nu_3+\nu_4$, but probably is to be identified with the former. In this case the inactive frequency ν_1 should lie at about 2191. The Raman spectrum of SiH_4 would definitely settle this question since it is to be expected that ν_1 would appear very strongly in that spectrum.

The complete spectrum will be discussed in a later communication when the grating curves have been extended to the other bands and a more exhaustive search for the less intense combination bands which will determine the value of the second inactive frequency ν_2.

We wish to acknowledge our indebtedness to Professor Warren C. Johnson of the Department of Chemistry at the University of Chicago, who has supplied us with the gas. A grant-in-aid awarded to us by the National Research Council is also acknowledged with appreciation.

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[1] E. K. Plyler and W. W. Sleator, Phys. Rev. **37**, 1493 (1931).

Note on Electric Moments and Infrared Spectra. A Correction

In connection with a recent article[1] under the above title, the writer greatly regrets having overlooked an article[2] by Bartholomé dealing with the above subject as applied to the hydrogen halides. Bartholomé has developed theory, and has made intensity measurements on the 0→1 bands of HCl, HBr, HI by a new and apparently improved method; he has made no intensity measurements on other bands, but finds the 0→2 band of HI qualitatively very weak. Bartholomé finds the intensity of the 0→1 band of HCl to be only about one-fourth as intense as the best previous data (Bourgin) indicated.

Combining Bartholomé's 0→1 intensity with Dunham's 0→2 intensity (which, however, although supposed to be more accurate than Bourgin's 0→1 intensity, was measured by the same method as the latter), one gets instead of Eq. (1) of reference 1 the following:

$$\mu_{HCl}\times 10^{18}=1.03\pm(0.52\xi+[-0.54\xi^2 \text{ or } +1.67\xi^2]).$$

The coefficient of ξ^2 was calculated by means of Dunham's equations.[3] Bartholomé's new data also permit writing equations for HBr and HI:

$$\mu_{HBr}\times 10^{18}=0.79\pm 0.51\xi+\cdots,$$
$$\mu_{HI}\times 10^{18}=0.38\pm 0.25\xi+\cdots.$$

The HI band, although weak, is stronger than previous work of Czerny indicated.

Bartholomé's data appear to be consistent with either of the two types of curves (Figs. 1*a*, 1*b*) shown in reference 1. Bartholomé gives a figure similar to Fig. 1*b*, with reasons for preferring this to the Fig. 1*a* or other types. Bartholomé shows theoretically that μ should increase as r^3 for r near zero. His argument that the $\mu(r)$ curve should rise, near

$r=0$, most rapidly for HI, least rapidly for HCl, causing the HI curve to have its maximum at smaller r than HBr or HCl, does not, however, seem convincing. As Bartholomé points out, quantitative intensity data on the various 0→2 bands, together with good frequency data on HI, might help greatly in determining the true form of the $\mu(r)$ curves.

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[1] R. S. Mulliken, J. Chem. Phys. **2**, 400 (1934). In Eq. (1) and the text, the possible values of the coefficient of ξ^2 in Eq. (1) should have been given as 0.035, 2.28 instead of 0.07, 4.56; the change is, however, unessential. In Figs. 1*a* and 1*b*, the μ scale should read 1.0 instead of 0.8, and other values in proportion; this, however, has no effect on the forms of the curves or on the discussion.
[2] E. Bartholomé, Zeits. f. physik. Chemie **B23**, 131 (1933).
[3] J. L. Dunham, Phys. Rev. **35**, 1347 (1930), Eq. (19). This paper seems to have been overlooked by Bartholomé.

Solutions Containing Zwitterions: Erratum

(J. Chem. Phys. **2**, 351, 1934).

Eq. (18) on page 355 should read

$$Q_n=\int\int\{\rho_0(r,\vartheta,\varphi)\,\rho_0(r',\vartheta',\varphi')\,r^n r'^n P_n(\cos\gamma)\}\,dv'dv$$

$$\cos\gamma=\cos\vartheta\cos\vartheta'+\sin\vartheta\sin\vartheta'\cos(\varphi-\varphi').$$

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On a Test for Free Radicals of Short Life

In the chemical investigation of free radicals of short life two major difficulties are encountered, first, their high rate of reaction, excluding all methods in which a gas is pumped out of the reaction vessel and analyzed afterwards, and secondly, closely connected with it, their small concentration. Actually, no characteristic chemical tests are known for free radicals as OH, NH, CH.

In the experiments to be described, the concentration of OH radicals present in the electric discharge through water vapor was observed by the intensity of their absorption spectrum. After interrupting the discharge, their gradual disappearance was traced by snapshots indicating the decay of their absorption spectrum with time.

The absorption spectrum of OH radicals has been observed in *thermally dissociated water vapor* at temperatures up to 1600°C by Bonhoeffer and Reichardt.[1] Various failures, however, to observe the same spectrum in *electric discharges* or *chemical reactions* have been reported in particular by Bonhoeffer and Pearson,[2] investigating the electric discharge through water vapor, and by Geib and Harteck[3] investigating various chemical reactions. It seems probable that the failures have in common the application of medium sized spectrographs. Actually, extremely high resolving power is required to observe a faint and sharp *absorption* line—contrary to the corresponding problem in *emission*. Hence in the present experiment the absorption spectrum was investigated in the second order of a 21-foot grating. This method is so sensitive that any carbon arc in air, without an absorption tube, shows the absorption spectrum of OH. Therefore the carbon arc has to be operated in dry nitrogen in order to provide the continuous background for the absorption experiment.

The electric discharge through water vapor was operated in series with a mechanical switch, turned by a synchronous motor, letting through one-half period of 60 cycle a.c. and interrupting through the following three halves, or, in other experiments, letting through one full period and interrupting the following 9 periods. A sector disk fixed on the same axis with the switch, rotating immediately in front of the slit of the spectrograph, screened off the inevitable emission spectrum of the discharge through water vapor and let through the continuous light from the carbon arc with the absorption spectrum for a brief snapshot after interrupting the discharge. The time interval between the breaking of the discharge and the snapshot could be varied by adjusting the phase of the sector disk on the axis with respect to the switch. This process of discharge and following snapshot went on periodically until an adequate total time of exposure was secured.

With the 21-foot grating the absorption spectrum of OH in the uninterrupted electric discharge through water vapor can be observed, provided that the continuous background is strong as compared with the emission of the discharge. It can be observed without this restriction after interrupting the discharge. These absorption bands of OH radicals show an intensity far above the minimum intensity observable with the present apparatus.

Their aspect, based on their intensity distribution, is different from the well-known OH emission bands. The strong heads, characteristic in emission, disappear in absorption. The reason is that in absorption the rotation of the OH molecules is low, determined by the temperature, whereas in emission much higher rotational quanta come out with great intensity. This difference has been interpreted in a recent paper.[4]

After interrupting the discharge a marked decay of the intensity of absorption was observed. The rate of reaction is such that after 1/8 sec. some absorption is left. This time limit was given by the present construction of the switch; it does not indicate the limit of the absorption spectrum observable.

The persistence of the absorption spectrum of OH radicals does not necessarily indicate a correspondingly long life of *OH radicals* after the interruption of the discharge. Instead, it might be that the average life of OH radicals is much shorter and that a new supply of OH is permanently reproduced by combination of O and H atoms so that actually the lifetime *of these atoms* is being observed.[5] It is hoped to decide this alternative by other experiments.

In order to study the kinetics of the OH radicals[6] a quantitative determination of their concentration will be attempted by photographic photometry.

The experiments discussed originated from H. N. Russell's[7] discussion of the absorption spectra of stellar atmospheres in which he mentioned the fact that the astronomer, restricted to the glass and part of the quartz region, is observing absorption spectra mainly of *unstable* molecules, whereas most *stable* molecules have their absorption spectra in the extreme ultraviolet. This property of unstable molecules suggested the application of the spectrograph to such reactions in gases.

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September 12, 1934.

[1] K. F. Bonhoeffer and H. Reichardt, Zeits. f. physik. Chemie **139**, 75 (1928).
[2] K. F. Bonhoeffer and T. G. Pearson, Zeits. f. physik. Chemie **14**, 1 (1931).
[3] P. Harteck, Trans. Faraday Soc. **30**, 139 (1934). Cf. W. Frankenburger and H. Klinkhardt, Zeits. f. physik. Chemie **15**, 440 (1931).
[4] O. Oldenberg, Phys. Rev. **46**, 210 (1934).
[5] This has been pointed out by Bonhoeffer and Pearson[2] discussing the afterglow of water vapor discovered by G. I. Lavin and F. B. Stewart (Proc. Nat. Acad. Sci. **15**, 829 (1929)).
[6] W. H. Rodebush and M. H. Wahl (J. Chem. Phys. **1**, 696 (1933)) obtained H_2O_2 as the principal product of the electric discharge through water vapor. Their hypothesis of a bimolecular association OH + OH $\rightarrow H_2O_2$ is based on the assumption of a very short life of OH.
[7] Russell, Lecture at the Harvard Observatory, 1931; Astrophys. J. **79**, 317 (1934).

The Raman Spectrum of Deuterio-Benzene (C_6D_6)

In order to facilitate the interpretation of the Raman spectrum of benzene, we have investigated the Raman spectrum of deuterio-benzene. Efforts were made to synthesize this material in our laboratory. An experiment with an exchange reaction between heavy water and benzene showed that no exchange took place in the vapor state at 450° in the presence of platinum black or between the two liquid phases which were in contact for ten days. An attempt to prepare deuterio-benzene by the polymerization of acetylene made from heavy water and calcium carbide yielded only about one cubic millimeter of liquid hydrocarbon from 3 cc of heavy water although the by-products were recovered and reprocessed several times. This indicates that the reaction with deuterio-acetylene gives a very small yield of benzene compared to the reaction with ordinary acetylene as judged by preliminary trial experiments and by the work of Zelinsky[1] on this reaction.

The material used in this investigation was loaned to us by Professor Zanetti of Columbia University who prepared it from heavy water of better than 99 percent purity by the polymerization of acetylene, working on a much larger scale. Due to the very small yield, the product could not be purified very thoroughly but a small amount of a liquid which smelled like benzene was obtained. The preparation of this material will be described elsewhere by Professor Zanetti. The liquid was distilled once in air over a water bath and then distilled into the Raman tube in vacuum, passing the vapors over P_2O_5 to remove traces of water.

The technique used for obtaining the Raman spectrum was that described by Murray and Andrews.[2] The Raman tube was made of Pyrex capillary of 1.2 mm bore fused to a Pyrex window. The length of the illuminated portion of the tube was 15 mm. Two spectra were obtained using the 4358 mercury line as the exciting light and one using the 4046 mercury line.

The two plates taken with the 4358 excitation showed a Raman line of 943 cm^{-1} displacement. Due to the very small size of the tube required, satisfactory elimination of parasitic light was impossible and the spectra were superimposed upon a rather strong continuous background which masked the other lines. Two other lines appeared to be present but are so weak as to be doubtful. These lines were at about 2290 excited by the 4046 line and 1600 excited by the 4358 line.

The selection rules for Raman spectra indicate that the 992 cm^{-1} line in benzene originates in a very symmetrical type of vibration. This suggests that it is due to the motion in which the six carbon atoms and the six carbon atoms attached to them move in and out along the lines drawn through the atoms to the center of the ring, all of the atoms vibrating in phase with each other. Other assignments have been suggested by various authors. The correctness of this assumption has been confirmed by studies with vibrating mechanical models of the two series of compounds: C_6H_6, $C_6H_5CH_3$, C_6H_5Cl, C_6H_5Br, C_6H_5I; and C_6H_6, C_6H_5Cl, *o*, *m*, and *p* $C_6H_4Cl_2$, (1, 2, 3), (1, 2, 4), and (1, 3, 5) $C_6H_3Cl_3$, and C_6Cl_6. The first of these series was studied by D. Teets, and the second by J. W. Murray and V. Deitz, the results being in process of publication in *The Journal of Chemical Physics*. In passing from compound to compound, the shifts of the mechanical frequency associated with the symmetrical expansion correspond exactly in sign and magnitude with the shifts observed in this strong line in the Raman spectra. Similar evidence indicates that the 3065 cm^{-1} line in benzene compounds corresponds to symmetrical expansion with the hydrogen atoms in a phase opposite to that of the carbon atoms.

On the basis of these correlations, a calculation may be made of the shift to be expected from the substitution of six deuterium atoms for the six hydrogen atoms in benzene. Let us assume that in this type of motion, the effect of the C−C bonds attached to one carbon atom is the same as if that carbon were attached by a bond to a fixed point in the center of the ring. Let S_I be the stretching force constant for this fictitious bond and S_{II} for the C−H bond. We may then define the motions of the atoms by the equations:

$$m_1 4\pi^2 \nu_\alpha^2 x_{\alpha 1} = S_I x_{\alpha 1} + S_{II}(x_{\alpha 1} - x_{\alpha 2}),$$
$$m_2 4\pi^2 \nu_\alpha^2 x_{\alpha 2} = S_{II}(x_{\alpha 2} - x_{\alpha 1}),$$

where $\alpha = 1$ or 2, $\nu_1 = 992.5$ cm^{-1}, $\nu_2 = 3065$ cm^{-1}, $m_1 = 12$ and $m_2 = 1.008$. Since the amplitude of the vibration is arbitrary, we may let $x_{\alpha 1} = 1$. Solving these equations simultaneously, we obtain $S_I = 7.55$ dynes cm^{-1}, and $S_{II} = 6.12$ dynes cm^{-1}. Using these values, we may let $m_2 = 2.016$ and solve for ν_1, obtaining a value of 945 cm^{-1}. The close agreement of this with the observed value indicates several things. First, it supports the assumed identity of the

material studied as deuterio-benzene. This was previously indicated by the method of preparation, the smell, and the general appearance of the Raman spectrum in which the only line which showed up distinctly bore the expected relation to the very strong 992 line of benzene. Secondly, assuming the spectrum to be that of C_6D_6, it supports the correlation of the two Raman lines with the assumed types of motion. Thirdly, it indicates that there is no appreciable change in the force constants of the bonds in benzene on account of the substitution of deuterium for hydrogen.

The authors acknowledge the invaluable cooperation of Professor Zanetti in furnishing the deuterio-benzene.

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September 5, 1934.

[1] Zelinsky, Ber. **57**, 264 (1924).
[2] J. W. Murray and D. H. Andrews, J. Chem. Phys. **1**, 406 (1933).